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Alignment of Hydrogen Molecules by High Pressure[*][†]

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Hydrogen molecules may be oriented by compressing solid hydrogen. If such orientation should prove practicable it would provide a mechanism producing very low temperatures by adiabatic compression of solid HD. The pressures necessary are estimated to be of the order of 10 000 atmos.

INTRODUCTION

It is well known that the H_2 molecule has a very wide separation of its rotational levels because of its very small moment of inertia. The ground state (angular momentum $J=0$) and the first excited state ($J=1$) are separated by an energy difference $\Delta E/k=170°\text{K}$. Compared with this level difference the evaporation energy of solid hydrogen at 0°K is much smaller, 183 cal/mole, which corresponds to 92°K in terms of degrees. The heat of fusion corresponds to only 14°K. From these facts Pauling[1] inferred that the H_2 molecules should be expected to rotate almost freely in the solid state. This view is supported by the observation of Raman lines in condensed hydrogen at frequencies which closely correspond to energy differences of the rotational states of *gaseous* hydrogen.[2] It can also be verified by an entirely theoretical argument based upon a calculation of the Van der Waals forces between hydrogen molecules that for the large mole volume of solid hydrogen[3] the anisotropy of the intermolecular forces[4] is far too insignificant to hold the molecules in any preferential orientation. The difference in potential energy between different orientations of one molecule in the field of its neighbors would be of the order of one millivolt, if the neighbors are unrealistically supposed fixed in position and orientation. This little anisotropy of the intermolecular force field could cause only a very small disturbance of the free rotational states, but could not produce a general orientation of the molecules.

By applying sufficiently high pressures, however, it ought to be possible to arrive at such a small mole volume that the anisotropy of the Van der Waals *repulsion* becomes the decisive factor in determining the molecular arrangement. Then the movement of the molecular axes, simply by lack of space, will be restricted to the neighborhood of well-defined orientations. The molecules will ultimately interlock and prevent each other by almost infinitely high potential barriers from flipping over into their inverse orientations.

TRANSFORMATION OF THE ROTATIONAL LEVELS

Figure 1 gives a qualitative scheme of the expected transformation of the rotational levels of a free H_2 molecule (left side of the scheme) to a state where the molecule is squeezed into a cavity more or less shaped by the space requirements of the molecule (right side). We suppose that the effective field of the neighbors forms a potential barrier at the angle $\vartheta=\pi/2$, where ϑ measures the deviation of the molecular axis from its equilibrium position. Furthermore we imagine the effective field to have axial symmetry around the axis of the cavity ($\vartheta=0$) and to be symmetric with respect to the plane $\vartheta=\pi/2$.

Then at any stage of the transformation the eigenfunctions can be classified by $|M|$, the absolute value of the rotational angular momentum in the direction of the axis of the cavity. Furthermore they have to be either symmetric or antisymmetric with respect to a reflection on the plane $\vartheta=\pi/2$. The antisymmetric functions have of course a node in the plane $\vartheta=\pi/2$.

In the limit of an *infinitely* high barrier, all eigenfunctions have to vanish at $\vartheta=\pi/2$. Those which originally had a node for $\vartheta=\pi/2$ will not be disturbed very much by the erection of this barrier. However, for all the other states the barrier will have the same effect as a new boundary condition and this will mean

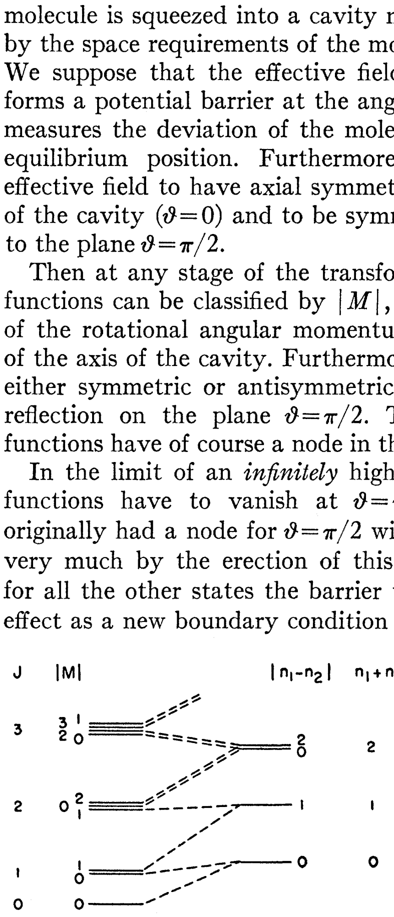

FIG. 1. Transformation of rotational states by compression.

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[†] This paper represents a slightly edited version of a manuscript left by the late Fritz London. He himself wanted to study the subject somewhat more before publication, but this was prevented by his untimely death. It has now been decided by a group of his friends and colleagues (M. J. Buckingham, W. M. Fairbank, H. Fröhlich, H. London, and L. W. Nordheim) that it would be preferable that this paper be published in this preliminary form rather than that a very original idea be lost.

The experimental possibilities mentioned in the paper were the subject of detailed discussions between London and W. M. Fairbank, and experiments to test the various aspects involved are in progress at Duke University.

[1] L. Pauling, Phys. Rev. **36**, 430 (1930).

[2] J. C. McLennan and J. H. McLeod, Nature **123**, 160 (1929).

[3] 22.65 cm³/mole, as given by F. Simon and H. Megaw, Nature **138**, 244 (1936). This means a molecular distance of 3.75 A, for which large value the zero-point energy of translational motion is mainly responsible; compare M. Hobbs, J. Chem. Phys. **7**, 318 (1939).

[4] See for example, Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954).

that their eigenvalue will rise, actually to the level of the next higher state with the same $|M|$, but which has already a node in the plane $\vartheta=\pi/2$ because it is antisymmetric with respect to the reflection on the plane $\vartheta=\pi/2$. Consequently, in the limit of a prohibitively large barrier all states will become doubly degenerate, each level originating from a symmetric and an antisymmetric state. In this limiting case the energy levels form the spectrum of a two-dimensional isotropic harmonic oscillator

$$E_{n_1,n_2}=(n_1+n_2+1)h\nu,$$

where $n_1, n_2=0, 1, 2, \cdots$, and the angular momentum M in the direction of the symmetry axis is given by

$$|M|=|n_1-n_2|,$$

whereas for the free molecule $|M|$ is subject to the well-known rule

$$|M|=0, 1, 2, \cdots, J.$$

The principle of continuity of symmetry defines an unambiguous coordination of the rotational states with those of the two-dimensional oscillator. This coordination is shown in Fig. 1 by the connecting lines. Actually, for solid hydrogen, we need consider only the two lowest states $J=0$ and $J=1$. All the other states would have an energy too large to be excited at solid hydrogen temperatures.

So far we have not yet considered the nuclear spin. It is well known that as a consequence of the Pauli principle the states with an even value of J (being symmetric with respect to an exchange of the space coordinates of the two protons) must have a resultant nuclear spin $I=0$ (parahydrogen). On the other hand, the states with an odd value of J are antisymmetric and consequently have a resultant spin $I=1$ and have thus the weight 3 corresponding to the three values $M_1=\pm 1, 0$ of the projection of I in a given direction (orthohydrogen). In the scheme of Fig. 1 we have omitted the level separation which is due to the nuclear spin-spin interaction, which is of the order 3×10^{-6} °K.

COOLING METHOD

The scheme shows that under sufficient compression in every case a parastate and a threefold orthostate coalesce to form a fourfold state. Thus, in particular the simple level of the ground state ($J=0$, $M=0$, $I=0$) coalesces with the threefold state $J=1$, $M=0$, $I=1$. Consequently, when the compression of solid parahydrogen is done isothermally and thermal equilibrium is reached, the entropy per mole of hydrogen has increased by $R\ \ln 4$; that means a heat $RT\ \ln 4$ must have been withdrawn from the surroundings. On the other hand, if the compression is done adiabatically, its temperature must fall to a value corresponding to the nuclear magnetic fine structure separation, that is, to about 3×10^{-6} °K.

However, it might not be easy to attain thermal equilibrium within a practicable time. It is well known that because of the symmetry of the H_2 molecule the ortho-para conversion proceeds normally very slowly. The possibility of the transition depends entirely on the presence of an inhomogeneous magnetic field. The conversion rate can be speeded up considerably by the presence of suitable paramagnetic substances. This problem would evidently require a future investigation by experiment.

For the unsymmetric HD molecule this obstacle to attaining thermal equilibrium does not exist. Each rotational state of HD has six nuclear spin states corresponding to the 2×3 orientations of the nuclear spins $\frac{1}{2}$ and 1 for H and D, respectively, and there is no special selection rule restricting the transitions. However, the very asymmetry of the molecule here sets a limit to the fusion of the levels $J=0$ and $J=1$. Since the HD molecule rotates or oscillates around its center of mass rather than its geometrical center, it will ultimately dig itself a cavity between its neighbors which will have no symmetry plane at $\vartheta=\pi/2$, unlike the case of the H_2 molecule. Consequently the two positions of the molecule in this cavity will have quite different energy levels. This spacing has nothing to do with the nuclear spin interaction.

Actually the asymmetry of the field is an effect of interaction and of rearrangement of the neighbors and can accordingly appear only *after* a kind of order-disorder transition has brought forth a preferential orientation for each molecule throughout the *whole* crystal. The realization of this orientation will presumably manifest itself by a kind of λ-point transition, in which the sign of $(\partial S/\partial P)_T$ would suddenly change from a positive to a negative value. However, *before* this transition is reached, the levels $J=0$ and $J=1$ might come very close to each other because the movement of each molecule must first be oscillatory before it can prefer one of the two orientations. The level separation will probably be much closer than the kT of liquid helium temperatures and in this case we would have a powerful cooling mechanism, though the temperature to be reached is not given in this case by the nuclear spin interaction. The entropy in question would be $R\ \ln 12-R\ \ln 6=R\ \ln 2$.

ESTIMATE OF THE PRESSURE REQUIRED

Recent measurements of the compressibility of solid H_2 and D_2 between 0 and 4000 kg/cm^2 at 4°K by Stewart and Swenson[5] may be used to estimate the minimum pressure required to arrest the rotational motion. They found that the compressibility of H_2 and D_2 decreases by a factor 10 when the pressure is increased from 0 to 2800 kg/cm^2, an unusually large decrease, which presumably is connected with the fact

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[5] J. W. Stewart and C. A. Swenson, Phys. Rev. **94**, 772 (1954) and **94**, 1069 (1954).

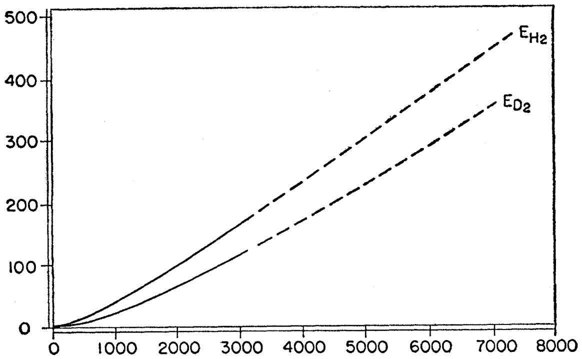

FIG. 2. Energy in cal/mole of solid H_2 and D_2 at 4°K as a function of pressure.

that the initial work of compression is mainly used to reduce space for the molecules by confining their rotational motion to a smaller angle rather than to drive the molecules deeper into their mutual Van der Waals repulsion field. Stewart and Swenson's measurements can be represented by the formula[6]

$$P=P_0(e^{(V_0-V)/b}-1),$$

with $V_0=22.65$ cm³/mole, $b=2.96$ cm³/mole, and $P_0=245$ kg/cm² for H_2; $V_0=19.56$ cm³/mole, $b=2.57$ cm³/mole, and $P_0=387$ kg/cm² for D_2; where V cm³/mole is the volume at pressure P kg/cm². This equation represents the data in their whole range within the experimental error. Using this formula we calculate the energy as a function of the volume and of the pressure (Fig. 2). We assume that for the low temperature of 4°K the thermal expansion coefficient vanishes,[7] $(\partial V/\partial T)_P \simeq 0$, and obtain:

$$\begin{aligned} E&=bP_0[e^{(V_0-V)/b}-(V_0-V)/b-1] \\ &=b[P-P_0\ln(1+P/P_0)]. \end{aligned} \tag{1}$$

For $P \gg P_0$, Eq. (1) gives the energy as an almost linear function of P.

In order to quench the rotational motion by compression an energy must be supplied *at least* sufficient to lift the ground state ($J=0$) to the level of the first excited rotational state ($J=1$). This means an energy of about 340 cal/mole for H_2 and 170 cal/mole for D_2. If the work of compression were entirely used for this purpose then, according to (1), a pressure of 5500 kg/cm² for H_2 and one of 4000 kg/cm² for D_2 and an intermediate value for HD would be needed. Actually a part of the energy of compression will of course be spent to overcome the Van der Waals repulsion. Moreover, the upper level ($J=1$) will also be disturbed by the compression of the solid; it will move toward higher values. Hence the above pressures are to be considered as lower limits. We would think that a pressure of the order of at least 10 000 kg/cm² would be needed to bring forth the entropy increase discussed above.

RADIO-FREQUENCY RESONANCE

In the case of HD, any molecular alignment by external pressure should be observable by the occurrence of a radio-frequency resonance. The spin interaction between the H and the D atoms belonging to the same molecule is given by the following Hamiltonian:

$$\mathcal{H}'=\frac{\mu_0^2 g_H g_D}{R^3}[\boldsymbol{\sigma}_{\frac{1}{2}}\cdot\boldsymbol{\sigma}_1-(3/R^2)(\boldsymbol{\sigma}_{\frac{1}{2}}\cdot\mathbf{R})(\boldsymbol{\sigma}_1\cdot\mathbf{R})]=\frac{\mu_0^2 g_H g_D}{R^3}\Omega,$$

where $\mu_0=5.049\times10^{-24}$ is the nuclear magneton; $g_H=5.587$ and $g_D=0.8576$ are the g-factors of the H and the D nucleus; $\mathbf{R}$ is the radius vector from one nucleus to the other one ($|\mathbf{R}|=R=0.75\times10^{-8}$ cm); $\boldsymbol{\sigma}_{\frac{1}{2}}$ and $\boldsymbol{\sigma}_1$ are the well-known operators of the spin angular momenta $\frac{1}{2}$ and 1 (in units of $\hbar$). The operator

$$\Omega=(\boldsymbol{\sigma}_{\frac{1}{2}}\cdot\boldsymbol{\sigma}_1)-3(\boldsymbol{\sigma}_{\frac{1}{2}}\cdot\mathbf{R})(\boldsymbol{\sigma}_1\cdot\mathbf{R})/R^2$$

has the three still twofold degenerate eigenvalues

$$\Omega=-1 \quad \text{for} \quad |m_1|=\tfrac{3}{2},$$
$$\Omega=\tfrac{1}{2}[1\pm\sqrt{3}] \quad \text{for} \quad |m_1|=\tfrac{1}{2}.$$

Furthermore we calculate the numerical factor in $\mathcal{H}'$:

$$\mu_0^2 g_H g_D/R^3 h=43.7 \text{ kc/sec}.$$

Accordingly there should be three characteristic frequencies at 27.7, 75.6, and 103.3 kc/sec.

This holds only for the case where the radius vector $\mathbf{R}$ has a sharply defined value which means in particular also a well-defined direction, so that the vector $\mathbf{R}$ can be considered as constant. Actually $\mathbf{R}$ is a dynamical variable, which is determined only statistically by a wave function, ψ. The latter, even if we consider the molecular distance R as approximately constant, will still depend on the angles ϑ and ϕ. Since $\mathcal{H}'$ is only a very small perturbation, we may regard $\psi(\vartheta,\phi)$ as approximately independent of $\mathcal{H}'$ and calculate the magnetic fine structure as given by the operator

$$\langle\mathcal{H}'\rangle_{\text{Av}}=\int\psi^*\mathcal{H}'\psi\sin\vartheta\, d\vartheta\, d\phi.$$

Suppose that the potential acting on a given molecule has axial symmetry and let ϑ be the angle between this symmetry axis and the axis of the molecule. Then we

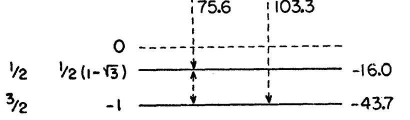

FIG. 3. Nuclear spin spectrum of oriented HD molecules.

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[6] The values given for the parameters have been altered slightly from those originally determined by Professor London in order to achieve better agreement with later experimental results which now extend to 10 000 kg/cm².

[7] Actually $(\partial V/\partial T)_P=-(\partial S/\partial P)_T$ must become negative for the pressures for which the energy levels coalesce. However, for small pressure $\partial V/\partial T$ will be positive and very small.

may write

$$\langle\Omega\rangle_{\mathrm{Av}}=[(\boldsymbol{\sigma}_{\frac{1}{2}}\cdot\boldsymbol{\sigma}_1)-3\zeta_{\frac{1}{2}}\zeta_1](\tfrac{3}{2}\langle\cos^2\vartheta\rangle_{\mathrm{Av}}-\tfrac{1}{2}),$$

where ζ_i is the z-component of the operator $\boldsymbol{\sigma}_i$ in a coordinate system which has the symmetry axis as z-axis. Evidently for entirely free molecules in the state $J=0$, which is well known to be isotropic, $\langle\cos^2\vartheta\rangle_{\mathrm{Av}}=\frac{1}{3}$ and hence

$$\langle\mathcal{H}'\rangle_{\mathrm{Av}}=0.$$

Consequently no resonance for the free rotating HD molecule in its ground state can be expected and indeed none has been found experimentally[8] in solid HD, another proof that in solid hydrogen the molecules are rotating practically as freely as in the gaseous state.

Any anisotropy which may be produced by compression could, however, be traced by the appearance of a radio-frequency resonance. The spectrum would be given by the eigenvalues of

$$\langle\mathcal{H}'/h\rangle_{\mathrm{Av}}=(\tfrac{3}{2}\langle\cos^2\vartheta\rangle_{\mathrm{Av}}-\tfrac{1}{2})\times 43.7\Omega \text{ kc/sec},$$

where Ω has the eigenvalues -1, $\frac{1}{2}(1\pm\sqrt{3})$. The frequency observed measures directly the degree of deviation from random orientation, that is the deviation of $\langle\cos^2\vartheta\rangle_{\mathrm{Av}}$ from the value $\frac{1}{3}$.

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

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Theory of Ionization Probability Near Threshold*

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The behavior of the cross section for ionization by electron impact is investigated in the vicinity of threshold by means of the quantum theory of inelastic scattering. A Coulomb-modified form of the Born approximation is used to calculate the S-wave ionization cross sections for H^+, He^+, and He^{++}. The electron-nuclear interaction is included in the unperturbed Hamiltonian for the problem while the interaction between the incident and atomic electrons is considered as the perturbation. It can be shown that the limiting law for the ionization of a hydrogen atom has a linear dependence on the excess incident energy. The absolute cross sections evaluated are in good agreement with experiment. Generalization of the excess energy dependence of the threshold law to the case of multiple (n-fold) ionization is found to yield the forms $E_{\mathrm{ex}}{}^n$ for ionization by electron impact and $E_{\mathrm{ex}}{}^{n-1}$ for photoionization.

I. INTRODUCTION

In recent years the development of techniques for obtaining better ionization threshold curves[1–3] has aroused interest in the theoretical side of this problem. Most previous calculations[4,5] of ionization cross sections by electron impact have attempted to explain the gross features of the ionization probability curve over a very large electron energy range (∼300 volts). In those cases the ordinary Born approximation was used to evaluate the direct ionization amplitude. The exchange amplitude was neglected since it is usually large only near the threshold.

Wannier[6] has derived a threshold law for single ionization which has the form of the 1.127th power of the excess energy. He obtained this via an approximate solution of the classical three-body problem coupled with certain statistical-mechanical arguments. A disadvantage of Wannier's result from an experimental point of view is that there is no way of knowing how far above the threshold this power law is supposed to be applicable. From a theoretical point of view, it appears more desirable to approach this problem within the conventional framework of the quantum theory of inelastic collisions so that all approximations made may be clearly delineated.

In the present calculation a modified form of the Born approximation is employed to obtain both the direct and exchange ionization (scattering) amplitudes. One *a priori* reason for expecting meaningful results from such a calculation is Wigner's[7] proof that the correct energy dependence of the cross section in the neighborhood of the threshold of a two-particle reaction is independent of the reaction mechanism but depends only on the long-range interaction of the product particles. In the concluding section we shall further discuss the justification for this procedure.

The method is here applied to the single ionization of hydrogen (atomic) and helium and to the double ionization of helium. Its formulation is described in detail for the hydrogen case. Its extension to helium follows in a parallel manner.

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[1] Foner, Kossiakoff, and McClure, Phys. Rev. 74, 1222 (1948).

[2] Fox, Hickam, Kjeldaas, and Grove, Phys. Rev. 84, 859 (1951).

[3] E. M. Clarke, Can. J. Phys. 32, 764 (1954).

[4] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) 140, 613 (1933).

[5] B. Yavorsky, Compt. rend. acad. sci. U.R.S.S. 49, 250 (1945).

[6] G. Wannier, Phys. Rev. 90, 817 (1953).

[7] E. P. Wigner, Phys. Rev. 73, 1002 (1948).