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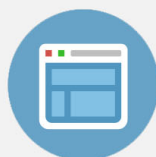J. Chem. Phys. 18, 1070 (1950); 10.1063/1.1747860

The Structure of H_3, H_3^+, and of H_3^-. IV

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In this paper, a direct calculation is made of the force constant for bending the nuclei in the triatomic hydrogen molecule, H_3, and in the ion, H_3^+, from a straight line. The neutral molecule has lower energy when the atoms are in a line rather than in neighboring triangular configurations. The opposite is true for the positive ion. The quantum-mechanical variational method is used together with the most general eigenfunctions which can be compounded from $1s$ hydrogen-like orbitals. The polar-homopolar composition of these eigenfunctions and the effective nuclear charge are varied simultaneously to give the lowest energy. For H_3, we obtain the force constant for bending, 15.88 kcal./radian^2, and the corresponding vibration frequency for bending, 3.26×10^{13} sec.$^{-1}$. These values agree well with those obtained by the semi-empirical scheme. The force constant for bending H_3^+ from a straight line is -15.41 kcal./radian^2. This negative value for the force constant indicates that the positive ion has lowest energy for triangular configurations, as predicted by Coulson. The energy of H_3^- is calculated for a linear symmetrical configuration. It is found that for reasonably small separations, H_3^- is unstable with respect to $H_2 + H^-$. At large separations H^- is attracted to H_2 to form a loose cluster but a rough calculation of the equilibrium constant indicates that $\dfrac{\text{Concentration } H_3^-}{\text{Concentration } H^-} = 0.2 \times \text{pressure } H_2$ in atmospheres. Thus at the low pressures which are used in the mass spectrograph, H_3^- could not be detected.

I N the previous communications of this series,[1-3] only the linear configurations of H_3 and of H_3^+ were considered. In this paper, a direct calculation is made of the force constant for bending the linear H_3 and H_3^+. Furthermore, we calculate the energy of linear H_3^- and find that the reason why this ion has never been observed experimentally is that it is energetically unstable with respect to $H_2 + H^-$. The force constant indicates that H_3 has a lower energy when the three nuclei are in a line as predicted by the first order perturbation method of London[4] and the semi-empirical scheme of Eyring and Polanyi.[5] This is quite different from the case of the triatomic hydrogen ion where the greatest binding energy is obtained for the triangular configurations. The reasons why H_3 should be linear and H_3^+ should be triangular have been discussed

by Coulson.[6] He uses the method of molecular orbitals to develop the following argument: "In H_3^+, we are only concerned with two electrons, and thus, in the ground state, only one type of orbital is filled: the two electrons will have the same space wave function but opposed spins. We are to choose that configuration of the nuclei which gives this orbital greatest binding energy. If a, b, c (Fig. 1) is the linear molecule, then the lowest orbital will only represent resonance between $a-b$ and $b-c$; the resonance $a-c$ is too small to make any appreciable contribution to the bonding. But in the triangular model, all three resonances contribute, and we may therefore expect greater bonding. In passing to the neutral molecule H_3, however, a new type of orbital has to be introduced having a node along the dotted line of the figure; this gives a bonding $a-b$ and $b-c$ but a repulsion $a-c$; there is therefore a definite tendency for this molecule to open out into a flat triangle or a straight line." The negative ion, H_3^-, has a greater tendency to flatten out than the H_3 since it has two electrons in the lowest orbital and the other two in the orbital with the node. Unfortunately Coulson's

[1] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. 4, 121 (1936).

[2] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. 4, 130 (1936).

[3] J. Hirschfelder, H. Diamond, and H. Eyring, J. Chem. Phys. 5, 695 (1937).

[4] F. London, Zeits. f. Physik 46, 455 (1928); 50, 24 (1928); *Probleme der Moderne Physik* (Hirzel & Co., 1928), p. 104.

[5] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie B12, 279 (1931).

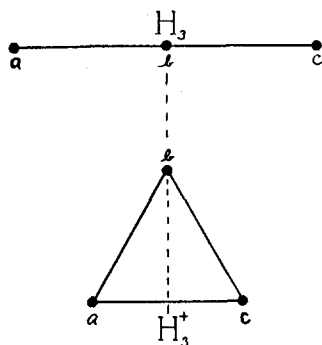[6] C. A. Coulson, Proc. Camb. Phil. Soc. 31(2), 244 (1935).

FIG. 1. H_3 is a linear molecule as shown by the upper diagram. H_3^+ is triangular as shown by the lower figure.

arguments do not constitute a rigorous proof; and it would be difficult to show, except by direct computations, that the increase in electronic binding energy more than compensates the hundreds of kilocalories increase in energy of nuclear repulsion when the H_3^+ is bent from a linear into a triangular configuration. Therefore, we determined to investigate the structure of the triatomic hydrogen molecule and ions using the variational method and the best eigenfunctions compounded from $1s$ hydrogen-like orbitals.

BENDING VIBRATION FREQUENCY FOR H_3

In order to obtain the vibration frequency for bending H_3 from the straight line, it is first necessary to compute the second derivative of the energy with the bending angle, θ (Fig. 2). This energy for various types of approximations has been expressed as an explicit function of a number of individual integrals.[7] The principal difficulty in this work was in obtaining the angle dependence of these integrals. Details of the mathematical analysis and the results are given in the appendix. It is a simple matter to substitute these integrals and their angle derivatives into the expressions for energy. The calculation of the energy for the Heitler-London[8] type of approximation will serve to illustrate the method which we employ. Consider the symmetrical configuration of the three hydrogen atoms such that the distance between nuclei a and b and between b and c is equal to R Bohr radii while the separation between nuclei a and c is equal to R_{ac}

[7] J. O. Hirschfelder, Dissertation, Princeton University (1935).

[8] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

Bohr radii. We shall designate Bohr radii by the symbol a_0. Fig. 2 shows this arrangement of the nuclei. From our previous work,[1, 7] the energy of the H_3 for the Heitler-London approximation is:

$$E = H/S, \qquad (1)$$

where $\quad S = 1 + I^2(R) - I^2(R_{ac}) - I^2(R)I(R_{ac}) \quad (2)$

and

$$
\begin{aligned}
Ha_0/e^2 = & S(2/R + 1/R_{ac} - 1.5) \\
& - 2G(R)[1 - I^2(R_{ac})] \\
& - [G(R) + G(R_{ac})][2 + I^2(R)] \\
& + [K(b, ac) + J(R_{ac})][2I(R_{ac}) + I^2(R)] \\
& - 2[K(a, bc) + J(R)][I(R) - I(R)I(R_{ac})] \\
& + 2L(aa, bb) + L(aa, cc) - L(ac, ac) + L(ab, ab) \\
& - 2I(R_{ac})L(bb, ac) + 2I(R)L(aa, bc) \\
& - 2I(R)L(ab, ac) - I(R_{ac})L(ab, bc).
\end{aligned}
\qquad (3)
$$

Here we have used the Rosen[9] notation:

$$I(R) = \pi^{-1} \int \exp(-r_{a1} - r_{b1}) d\tau_1,$$

$$I(R_{ac}) = \pi^{-1} \int \exp(-r_{a1} - r_{c1}) d\tau_1,$$

$$G(R) = \pi^{-1} \int (r_{b1})^{-1} \exp(-2r_{a1}) d\tau_1,$$

$$G(R_{ac}) = \pi^{-1} \int (r_{c1})^{-1} \exp(-2r_{a1}) d\tau_1,$$

$$J(R) = \pi^{-1} \int (r_{b1})^{-1} \exp(-r_{a1} - r_{b1}) d\tau_1,$$

$$J(R_{ac}) = \pi^{-1} \int (r_{a1})^{-1} \exp(-r_{a1} - r_{c1}) d\tau_1,$$

$$K(a, bc) = \pi^{-1} \int (r_{a1})^{-1} \exp(-r_{b1} - r_{c1}) d\tau_1,$$

$$K(b, ac) = \pi^{-1} \int (r_{b1})^{-1} \exp(-r_{a1} - r_{c1}) d\tau_1,$$

$$L(\alpha\beta, \gamma\delta) = \pi^{-2} \int \int (r_{12})^{-1}$$

$$\times \exp(-r_{\alpha1} - r_{\beta1} - r_{\gamma2} - r_{\delta2}) d\tau_1 d\tau_2,$$

(4)

where α, β, γ, δ may stand for the position of the

[9] N. Rosen, Phys. Rev. **38**, 255 (1931); **38**, 2099 (1931).

nuclei a, b, c. The second derivative of the energy, E, with respect to the bending angle, θ, is

$$\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0} = \frac{1}{S}\left(\frac{\partial^2 H}{\partial \theta^2}\right)_{\theta=0} - \frac{H}{S^2}\left(\frac{\partial^2 S}{\partial \theta^2}\right)_{\theta=0} \quad (5)$$

All of the integrals which are functions of $R_{ac} \equiv 2R \cos(\theta/2)$ as well as the integrals: $K(b, ac)$, $K(a, bc)$, $L(aa, cc)$, $L(ac, ac)$, $L(bb, ac)$, $L(aa, bc)$, $L(ab, ac)$, and $L(ab, bc)$ are functions of θ. The second derivatives of these integrals with respect to θ are discussed in the appendix. When we substitute the values of these derivatives for the best separation of the nuclei, $R = 2.0a_0$, into (5), we obtain:

$$\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0} = 14.75 \text{ kcal./radian}^2 = 1.018$$

$$\times 10^{-12} \text{ ergs/radian}^2. \quad (6)$$

Since $(\partial^2 E/\partial \theta^2)_{\theta=0}$ is positive, H_3 is more stable in the linear configuration than when the nuclei are bent from the line. The vibration frequency for bending, ν_θ, corresponding to this force constant is[7]

$$\nu_\theta = (\pi R)^{-1}\left(\frac{3}{2m_H}\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0}\right)^{\frac{1}{2}} = 2.89 \times 10^{13} \quad (7)$$

and $h\nu_\theta = 2.74$ kcal.

A better approximation to the energy of the triatomic molecule is obtained by varying the effective nuclear charge, z, or the screening constant, $z-1$, so as to obtain the lowest energy. This variation leads to the Wang[10] type of approximation and can be carried out very easily without the calculation of any additional integrals. When the effective nuclear charge is introduced, the energy becomes[1, 7]

$$E_z = zE_{z=1} + z(z-1)A/S, \quad (8)$$

where

$$A = 3/2 - \tfrac{1}{2}I^2(R) + 2J(R)I(R) + \tfrac{1}{2}I^2(R_{ac})$$
$$- 2I(R_{ac})J(R_{ac}) + (3/2)I(R_{ac})I^2(R)$$
$$- I^2(R)J(R_{ac}) - 2I(R)I(R_{ac})J(R). \quad (9)$$

Here R and R_{ac} now stand for z times the actual
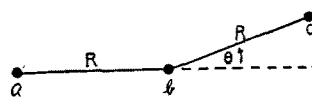
¹⁰ S. C. Wang, Phys. Rev. 31, 579 (1928).

FIG. 2. θ is the angle of bending of the molecule from the straight line. The separations between nuclei a and b and between nuclei b and c are equal to Ra_0 where a_0 is the length of the Bohr radius.

nuclear separations. Taking the second derivative of (8) with respect to θ and using the best value of z $(z=1.05864)$ for the best separation between nuclei, $r_{ab} = R/z = 1.889a_0$:

$$\left(\frac{\partial^2 E_z}{\partial \theta^2}\right)_{\theta=0} = 18.04 \text{ kcal./rad.}^2$$

$$= 1.245 \times 10^{-12} \text{ ergs/rad.}^2.$$

From which it follows that

$$\nu_{\theta \text{ Wang App.}} = 3.370 \times 10^{13}$$
and $\qquad h\nu_{\theta \text{ Wang App.}} = 3.20$ kcal.

The binding energy becomes a very complicated function of the individual integrals when the eigenfunction is taken to be the best linear combination of the homopolar function and the three polar states which are antisymmetric with respect to a permutation of the nuclei a and c. However, the procedure for computing the bending frequency remains the same as for the simpler Heitler-London approximation. Thus we find for the Heitler-London plus-polar states approximation:

$$\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0} = 11.11 \frac{\text{kcal.}}{\text{rad.}^2}, \quad \nu_\theta = 2.508 \times 10^{13},$$

$$h\nu_\theta = 2.38 \text{ kcal.}$$

Now varying the effective nuclear charge to form the Wang plus-polar states approximation:

$$\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0} = 15.88 \frac{\text{kcal.}}{\text{rad.}^2}, \quad \nu_\theta = 3.26 \times 10^{13},$$

$$h\nu_\theta = 3.09 \text{ kcal.}$$

Thus in all four approximations, the energy of H_3 is lower for the linear than for the neighboring triangular configurations. However we cannot rule out the possibility of the energy of H_3 having more than one minimum when it is plotted as a function of θ. A direct calculation of the energy

TABLE I. *Bending frequencies for the vibration of H_3 calculated in a number of different ways.*

	$(\partial^2 E/\partial\theta^2)_{\theta=0}$	ν_θ	$h\nu_\theta$	E	r_{ab}
Heitler-London Approx.	$14.75 \frac{\text{kcal.}}{\text{rad.}^2}$	2.89×10^{13} sec.$^{-1}$	2.74 kcal.	-53.1 kcal.	$2.0a_0$
Wang Approx.	18.04	3.37	3.20	-56.2	1.89
H. L. Plus-Polar States Approx.	11.11	2.51	2.38	-60.4	2.00
Wang Plus-Polar States Approx.	15.88	3.26	3.09	-67.1	1.84
Semi-Empirical (20% Coulombic)	10.93	2.70	2.56	-102.2	1.84

for the equilateral triangular configuration will be made as soon as possible.

Beside the ground state of the H_3 molecule which is antisymmetric with respect to a permutation of the nuclei a and c, there is an excited state which is symmetric with respect to such a permutation. If we consider only the homopolar eigenfunctions, this excited state corresponds to a bond between the widely separated nuclei a and c. The energy of this state is such as to make the atoms repel each other at all separations. It is interesting to find that such a repulsive state has its lowest energy for the linear configuration and its bending vibration frequency is similar to that for the ground state. We calculate: (repulsive state, Heitler-London approximation)

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0} = 10.00 \frac{\text{kcal.}}{\text{rad.}^2}, \quad \nu_\theta = 2.38\times10^{13},$$

$$h\nu_\theta = 2.26 \text{ kcal.}$$

The results which we have obtained for the triatomic molecule by the variational method are in excellent agreement with those calculated by the semi-empirical scheme of Eyring and his co-workers[11] In that treatment, the energy of the symmetrical H_3 is

$$E = 3E_{\text{H}} + (1+n)w(r_{ab}) - (1-2n)w(r_{ac}). \quad (10)$$

Here $E_{\text{H}} = -\frac{1}{2}e^2/a_0$ is the energy of the separated hydrogen atoms, $w(r_{ab})$ and $w(r_{ac})$ are the Morse curve potential energies for normal hydrogen molecules in which the nuclei are separated a distance r_{ab} and r_{ac} respectively, i.e.

$$w(r_{ab}) = D'[\exp\ (-2a(r_{ab}-r_0)) - 2 \exp\ (-a(r_{ab}-r_0))], \quad (11)$$

where D' is the energy of dissociation of the

[11] See, for example, J. Hirschfelder, H. Eyring, and B. Topley, J. Chem. Phys. 4, 170 (1936) or Appendices 3 and 4 in the dissertation of one of us (J.O.H., reference 7).

normal H_2 plus the zero-point energy, r_0 is the equilibrium separation for the diatomic molecule, and a is a constant determining the curvature of the potential energy. For H_2: $D' = 108.8$ kcal., $a = 1.94\times10^8$ cm^{-1}, $r_0 = 0.75\times10^{-8}$ cm. In Eq. (10), n is the so-called fraction of Coulombic energy. According to the first-order perturbation theory, the total binding energy, $w(r_{ab})$, of a diatomic molecule is the sum of a Coulombic part and another term, the exchange energy, which is a function of the electronic binding state. In the Eyring scheme, the Coulombic energy is $nw(r_{ab})$ and for best results n is usually taken to be 0.20. The principal justification of the semi-empirical scheme arises from the agreement which is obtained with the experimentally measured activation energy for a large number of cases. From Eq. (10) it follows that

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0} = -(1-2n)\left(\frac{\partial^2 w(r_{ac})}{\partial\theta^2}\right)_{\theta=0}$$

$$= (1-2n)D'ar_{ab}[\exp\ (-a(r_{ac}-r_0)) - \exp\ (-2a(r_{ac}-r_0))]. \quad (12)$$

Taking $n = 0.20$ and $r_{ab} = 1.84a_0$, we obtain:

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0} = 10.93 \frac{\text{kcal.}}{\text{rad.}^2}, \quad \nu_\theta = 2.70\times10^{13},$$

$$h\nu_\theta = 2.56 \text{ kcal.}$$

Table I shows all of the results which are obtained from both the semi-empirical and the variational method calculations. The agreement is surprisingly good and gives a further justification for the use of the semi-empirical scheme.

FORCE CONSTANT FOR BENDING H_3^+

The force constant for bending H_3^+ from the straight line is calculated in exactly the same

manner by the variational method as for the case of the neutral molecule. The same integrals occur in both problems and these may be substituted into the explicit expressions which we have derived for the energy.[2, 7] Since the polar states are of great importance in the charge distribution of $H_3{}^+$, we consider immediately the Heitler-London plus-polar states and the Wang plus-polar states approximations. In the former case,

$$\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0} = -9.96\frac{\text{kcal.}}{\text{rad.}^2}$$

and in the latter, $-15.41\dfrac{\text{kcal.}}{\text{rad.}^2}$ (see Table II).

Since the force constant is negative for both approximations, the triatomic ion is more stable when the nuclei are in a triangle than when they form a straight line. This result, as was mentioned previously, is in accord with the expectations of Coulson.[6] A direct calculation of the energy of $H_3{}^+$ for the equilateral triangular configuration will be made as soon as the necessary integrals are evaluated.

From the variational method calculations of the energy required to bend H_3 and $H_3{}^+$ through an infinitesimal angle from the straight line, we see that H_3 has the lowest energy for the linear and $H_3{}^+$ for the triangular configurations. Thus it is energetically easier for a hydrogen atom to approach a hydrogen molecule along the line of nuclei; but the most favorable approach of a proton to a hydrogen molecule is along a path perpendicular to this line of nuclei.

The Energy of $H_3{}^-$

At large separations, an ion is attracted to a neutral molecule by ionic polarization forces. When a proton, H^+, approaches a hydrogen molecule, H_2, a stable ion, $H_3{}^+$, is formed. The question arises as to whether when H^- approaches H_2, a stable molecular ion $H_3{}^-$ is formed. Ions of the type $X_3{}^-$ are observed for the halogens in the mass spectrograph,[12] but $H_3{}^-$ has never been discovered. In a previous communication[13] it was shown that the diatomic

[12] For example $I_3{}^-$, Hogness and Harkness, Phys. Rev. 32, 784 (1928).
[13] H. Eyring, J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys. 4, 479 (1936).

hydrogen ion, $H_2{}^-$ is unstable. In this treatment we treat $H_3{}^-$ by means of the quantum mechanical variational method and we find that the energy corresponds to a strong repulsion between H^- and H_2 at small separations. The minimum energy for $H_2 + H^-$, just as for $H + H^-$, is of the order of a few calories binding and occurs for large separations.

The energy of $H_3{}^-$ is calculated using the most general linear combination of states which can be formed from $1s$ hydrogen-like orbitals. We consider the symmetrical linear configuration for $r_{ab} = r_{bc} = 2.0 a_0/z$. (See Fig. 2 where $\theta = 0$.) Here z is the effective nuclear charge in the eigenfunctions, as in the other examples which we have just considered. Since the Hamiltonian is symmetrical with respect to nuclei a and c, it follows that those eigenfunctions which are symmetric with respect to a permutation of a and c are noncombining or orthogonal with respect to those that are antisymmetric in this sense. There are four symmetric eigenfunctions which can be formed from the $1s$ hydrogen-like orbitals:

$$
\begin{aligned}
\chi_1 &= \begin{pmatrix} a & a & b & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} a & a & b & c \\ \alpha & \beta & \beta & \alpha \end{pmatrix} \\
&\quad + \begin{pmatrix} c & c & a & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} c & c & a & b \\ \alpha & \beta & \beta & \alpha \end{pmatrix}, \\
\chi_2 &= \begin{pmatrix} b & b & a & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} b & b & a & c \\ \alpha & \beta & \beta & \alpha \end{pmatrix}, \\
\chi_3 &= \begin{pmatrix} a & a & b & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix} + \begin{pmatrix} c & c & b & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix}, \\
\chi_4 &= \begin{pmatrix} a & a & c & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix}.
\end{aligned}
\tag{13}
$$

Here the quantities in parenthesis indicate the usual Slater determinants and α and β are the two eigenfunctions corresponding to the eigenvalues $h/4\pi$ and $-h/4\pi$ for the z component of electron spin. The state χ_1 corresponds to a resonance between the configuration with two electrons on a and the other two electrons forming the bond

TABLE II. *Force constant for bending $H_3{}^+$ from a straight line.*

	$(\partial^2 E/\partial \theta^2)_{\theta=0}$	$E - 2E_H$	r_{ab}
Heitler-London Plus-Polar States Approx.	$-9.96\ \dfrac{\text{kcal.}}{\text{rad.}^2}$	-108.6 kcal.	$2.00\ a_0$
Wang Plus-Polar States Approx.	-15.41	-155.4	1.52

TABLE III. *Energy of H_3^-. These energies are given with reference to three hydrogen atoms and an electron all infinitely far apart.*
$r_{ab} = r_{bc} = 2.0\ a_0/z$

	Energy H_3^- $-$ 3 Energy H	
Symmetric States		
(symmetric with respect to an interchange of a and c)		
Heitler-London Approx.	-26.2	kcal./mole
Wang Approximation	-41.1	($z = 0.89$)
H.L. Plus-Polar Approx.	-30.3	
Wang Plus-Polar Approx.	-43.7	($z = 0.89$)
Antisymmetric States		
Heitler-London Approx.	$+300$	

$b-c$ and the configuration with two electrons on c and the other two forming the bond $a-b$. The state χ_2 corresponds to two electrons on b one on a and one on c forming the bonds $a-b$ and $b-c$. The states χ_3 and χ_4 are pure polar states. There are two antisymmetrical eigenfunctions:

$$\chi_5 = \begin{pmatrix} a & a & b & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} a & a & b & c \\ \alpha & \beta & \beta & \alpha \end{pmatrix}$$
$$- \begin{pmatrix} c & c & a & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix} + \begin{pmatrix} c & c & a & b \\ \alpha & \beta & \beta & \alpha \end{pmatrix}, \quad (14)$$
$$\chi_6 = \begin{pmatrix} a & a & b & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} c & c & b & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix}.$$

The symmetrical states give the lowest energy. This is to be expected from the molecular orbital point of view. The lowest molecular orbital for an electron in the field of three hydrogen nuclei is symmetrical in a and c. The orbital corresponding to the first excited state has a node through b and is antisymmetrical with respect to a permutation of a and c. The positive ion, H_3^+, has two electrons in the lowest orbital and is therefore symmetrical in a and c. The neutral molecule has one electron in the excited state and is antisymmetrical. The negative ion has two electrons in the excited state and is symmetric since the product of the two antisymmetrical functions is symmetrical.

Taking $\Psi = A_1\chi_1 + A_2\chi_2$ as the eigenfunction and varying the constants A_1 and A_2 so as to get the lowest energy, we get a Heitler-London type of approximation. By varying the effective nuclear charge, z, simultaneously with the A's, we obtain a Wang type of approximation. The inclusion of the polar states does not affect the results appreciably. Table III shows the values which we obtain. The greatest binding energy for the three hydrogen atoms and the electron in the

configuration which we consider is 43.7 kcal. Since an electron is bound to a hydrogen atom in H^- with 16.5 kcal. and the two hydrogen atoms in H_2 are held together by 92.2 kcal. to the approximation of our calculations, we see that our configuration of H_3^- will dissociate into $H_2 + H^-$ giving off an energy $16.5 + 92.2 - 43.7 = 65.0$ kcal. From this result it is apparent that H_3^- is analogous to H_2^-. At large separations, H^- is attracted to H_2; at small separations it is repelled. For some large separation there will be a minimum for the energy of the system with possibly a few discrete vibrational and rotational states corresponding to a stable H_3^- molecule. Entropy considerations will favor the decomposition of H_3^- and we can make a rough calculation or estimate of the ratio of H_3^- to H^- which should be present at equilibrium on the assumption that H_3^- is a loose cluster with the H^- held to the H_2 by ionic-polarization forces. This calculation is identical with the one which has already been given for other clusters in hydrogen.[13] Using Eq. (12) of that reference we see that if the H^- is separated a distance of 2.8 angstrom from the H_2 at room temperature.[14]

$$\frac{\text{Concentration } H_3^-}{\text{Concentration } H^-} = 0.2 \times \text{pressure } H_2 \text{ in atmospheres.} \quad (15)$$

Thus under the conditions of the mass spectrograph, i.e., pressures under a thousandth of an atmosphere, it would be extremely difficult to detect H_3^- which would be present in less than $1/5000$ the concentration of the H^-. The above estimate should be accurate as to order of magnitude.

APPENDIX

Integrals

The principal difficulty in obtaining the energy of a molecule by the variational method is due to the complicated nature of the integrals which arise when even a simple form for the charge distribution is assumed. In all of the calculations which we have made for H_3 and H_3^+, the eigenfunctions have been compounded from $1s$ hydrogen-like orbitals. The energy is then expressed in terms

[14] The assumption is made that the frequency of vibration of the H_2 with respect to H^- is 100 cm^{-1} which is a reasonable magnitude. If some other value were taken for this frequency, the results would not be appreciably changed.

of the I, G, J, K, and L integrals defined in Eq. (4). All of these integrals except the four three-center multiple exchange integrals: $L(aa, bc)$, $L(bb, ac)$, $L(ab, ac)$, and $L(ab, bc)$ are known for all configurations of the nuclei and there is little difficulty in obtaining the second derivatives of these integrals with respect to θ. Thus if we designate the operator $(\partial^2/\partial\theta^2)_{\theta=0}$ by the superscript ":

$$I''(R_{ac}) = (1/3)(R^2 + 2R^3) \exp(-2R),$$
$$J''(R_{ac}) = R^2 \exp(-2R),$$
$$G''(R_{ac}) = \tfrac{1}{4}G(2R) - (R + \tfrac{1}{4})\exp(-4R),$$
$$L''(aa, ac) = (1/16)[\{16R^2 - 7R + (5/4) + (5/8R)\}$$
$$\times \exp(-2R) - \{3R + (15/4)$$
$$+ (5/8R)\}\exp(-6R)],$$
$$L''(aa, cc) = \tfrac{1}{4}L(aa, cc) - [(5/32) + (5/8)R + R^2$$
$$+ (2/3)R^3]\exp(-4R),$$
$$L''(ac, ac) = \tfrac{1}{4}L(ac, ac) + (2/5)(R + 2R^2) \quad (16)$$
$$\times \{C + \log(2R)\}I(2R)\exp(-2R)$$
$$+ (2/5)(R - 2R^2)F(2R)Ei(-8R)\exp(+2R)$$
$$- (2/5)(2R - (16/3)R^3)Ei(-4R)$$
$$- [(5/32) + (5/8)R + \tfrac{1}{2}R^2 + (28/15)R^3$$
$$+ (8/15)R^4]\exp(-4R),$$
$$K''(c, ab) = -2K(c, ab) + (2R)^{-1}$$
$$\times [3I(R) - (3 + 5R + R^2)\exp(-3R)],$$
$$K''(b, ac) = \tfrac{1}{2}K(b, ac) + \tfrac{1}{4}R(1 + 2R)(C + \log(4R))$$
$$\times \exp(-2R) - \tfrac{1}{4}R(1 - 2R)\exp(+2R)Ei(-4R)$$
$$- (\tfrac{1}{2} + R + R^2)\exp(-2R).$$

In these equations, $Ei(-x)$ is the integral logarithm[15] defined by the relation $Ei(-x) = -\int_x^\infty x^{-1}\exp(-x)dx$. C is the transcendental $0.577215665\cdots$. The other new function introduced is

$$F(2R) = (1 - 2R + (4/3)R^2)\exp(+2R).$$

The computation of the second derivatives of the three-center multiple exchange integrals is much more difficult. Each of these involve θ through the factor $\exp(-r_{c2})$ in the integrand. If we use the ellipsoidal coordinates with a and b as foci:

$$\lambda_2 = (r_{a2} + r_{b2})/R, \quad \mu_2 = (r_{a2} - r_{b2})/R, \quad \phi_2 \quad (17)$$

it follows that

$$r_{c2} = \tfrac{1}{2}R[(\lambda_2^2 + \mu_2^2 - 6\mu_2\lambda_2 + 8) - 8\cos\phi\cos(\theta/2)$$
$$\times (1 - \cos^2(\theta/2))^{\frac{1}{2}}((\lambda_2^2 - 1)(1 - \mu_2^2))^{\frac{1}{2}}$$
$$+ 8(1 - \cos^2(\theta/2))(\mu_2\lambda_2 - 1)]^{\frac{1}{2}}. \quad (18)$$

The form of r_{c2} is of such a complicated nature that it would be necessary to carry out the integrations over λ_2, μ_2, ϕ_2 numerically for the three-center multiple exchange integrals whenever θ is not zero. From (18) it may be shown that:

$$\left(\frac{\partial^2}{\partial\theta^2}\exp(-r_{c2})\right)_{\theta=0} = \exp(-r_{c2})[\tfrac{1}{4}R^4(r_{c2}^{-2} + r_{c2}^{-3})$$
$$\times (\lambda_2^2 - 1)(1 - \mu_2^2)\cos^2\phi_2 - \tfrac{1}{2}R^2 r_{c2}^{-1}(\mu_2\lambda_2 - 1)]. \quad (19)$$

For this case, r_{c2} is not a function of ϕ_2, since θ in (18) is set equal to zero.

The four three-center multiple exchange integrals are

$$L(aa, bc) = \pi^{-2}\int\int (r_{12})^{-1}\exp(-2r_{a1} - r_{b2} - r_{c2})d\tau_2 d\tau_1,$$
$$L(bb, ac) = \pi^{-2}\int\int (r_{12})^{-1}\exp(-2r_{b1} - r_{a2} - r_{c2})d\tau_2 d\tau_1,$$
$$\quad (20)$$
$$L(ab, ac) = \pi^{-2}\int\int (r_{12})^{-1}\exp(-r_{a1} - r_{b1} - r_{a2} - r_{c2})d\tau_2 d\tau_1,$$
$$L(ab, bc) = \pi^{-2}\int\int (r_{12})^{-1}\exp(-r_{a1} - r_{b1} - r_{a2} - r_{c2})d\tau_2 d\tau_1.$$

In each of these cases the integration can be carried out over the coordinates of electron 1 regardless of the position of the nuclei. It will be noticed that the only dependence of these integrals on θ is through the $\exp(-r_{c2})$ factor in the integrand, so that this integration over the first electron is independent of θ. Remembering that

$$G(r_{a2}) = \pi^{-1}\int (r_{12})^{-1}\exp(-2r_{a1})d\tau_1 = (r_{a2})^{-1}$$
$$- (1 + (r_{a2})^{-1})\exp(-2r_{a2}),$$
$$G(r_{b2}) = \pi^{-1}\int (r_{12})^{-1}\exp(-2r_{b1})d\tau_1 \quad (21)$$
$$= r_{b2}^{-1} - (1 + r_{b2}^{-1})\exp(-2r_{b2}),$$
$$K(2, ab) = \pi^{-1}\int (r_{12})^{-1}\exp(-r_{a1} - r_{b1})d\tau_1,$$

the three-center multiple exchange integrals become:

$$L(aa, bc) = K(a, bc) - T(a, bc),$$
$$T(a, bc) = \pi^{-1}\int (1 + r_{a2}^{-1})\exp(-2r_{a2} - r_{b2} - r_{c2})d\tau_2,$$
$$L(bb, ac) = K(b, ac) - T(b, ac),$$
$$T(b, ac) = \pi^{-1}\int (1 + r_{b2}^{-1})\exp(-2r_{b2} - r_{a2} - r_{c2})d\tau_2, \quad (22)$$
$$L(ab, ac) = \pi^{-1}\int K(2, ab)\exp(-r_{a2} - r_{c2})d\tau_2,$$
$$L(ab, bc) = \pi^{-1}\int K(2, ab)\exp(-r_{b2} - r_{c2})d\tau_2.$$

It is again convenient to use the ellipsoidal coordinates (17) in which the volume element is

$$d\tau_2 = (R^3/8)d\lambda_2 d\mu_2 d\phi_2(\lambda_2^2 - \mu_2^2).$$

Now differentiating the integrands with respect to θ and making use of (19), we obtain:

$$T''(a, bc) = \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 P(1 + (\tfrac{1}{2}R(\lambda_2 + \mu_2))^{-1})$$
$$\times \exp(-\tfrac{1}{2}R(3\lambda_2 + \mu_2))d\mu_2 d\lambda_2,$$
$$T''(b, ac) = \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 P(1 + (\tfrac{1}{2}R(\lambda_2 - \mu_2))^{-1})$$
$$\times \exp(-\tfrac{1}{2}R(3\lambda_2 - \mu_2))d\mu_2 d\lambda_2, \quad (23)$$
$$L''(ab, ac) = \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 PK(2, ab)$$
$$\times \exp(-\tfrac{1}{2}R(\lambda_2 + \mu_2))d\mu_2 d\lambda_2,$$
$$L''(ab, bc) = \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 PK(2, ab)$$
$$\times \exp(-\tfrac{1}{2}R(\lambda_2 - \mu_2))d\mu_2 d\lambda_2,$$

where

$$P = (2\pi)^{-1}(\lambda_2^2 - \mu_2^2)\int_0^{2\pi}\left(\frac{\partial^2}{\partial\theta^2}\exp(-r_{c2})\right)_{\theta=0}d\phi_2$$
$$= \exp(-r_{c2})(\lambda_2^2 - \mu_2^2)[(R^4/8)(r_{c2}^{-2} + r_{c2}^{-3})$$
$$\times (\lambda_2^2 - 1)(1 - \mu_2^2) - \tfrac{1}{2}R^2 r_{c2}^{-1}(\mu_2\lambda_2 - 1)]. \quad (24)$$

These integrands are evaluated numerically for $R = 2.0a_0$

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[15] See for example, Jahnke and Emde, *Tables of Functions*, second edition (Teubner 1933), p. 78.

at over a hundred points and the integrations are performed graphically with the aid of a planimeter. When $\lambda_2 = 3$, $\mu_2 = 1.0$ (i.e. $r_{c2} = 0$) the integrands become infinite and it is necessary to carry out the integrations analytically in this region. The accuracy of the numerical integrations is considerably decreased by a partial cancellation of positive and negative contributions to the integrals. However, we believe that we have obtained sufficient accuracy for the purposes of this paper. The following is a summary of the numerical values of the second derivatives of the integrals which we used:

(Numbers in units of e^2/a_0 for $R = 2.0a_0$)

$$L''(aa, bc) = 0.029921, \quad L''(bb, ac) = 0.052345,$$
$$L''(ab, ac) = 0.033504, \quad L''(ab, bc) = 0.000248,$$
$$L''(ac, ac) = 0.021646, \quad L''(aa, cc) = 0.058286,$$
$$L''(aa, ac) = 0.059021, \quad K''(a, bc) = 0.035949,$$
$$K''(b, ac) = 0.058053, \quad J''(R_{ac}) = 0.073263,$$
$$G''(R_{ac}) = 0.061640, \quad I''(R_{ac}) = 0.122104.$$

A Mechanical Analyzer for the Solution of Secular Equations and the Calculation of Molecular Vibration Frequencies

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A set of coupled harmonic oscillators has been constructed, so designed that it can be used to solve the numerical secular equations occurring in the theory of the vibration of polyatomic molecules and in other problems. Each oscillator consists of a shaft with cross arms carrying weights to increase the moment of inertia and springs to provide restoring force. The unit is free to rotate about the axis of the shaft, except for the restoring force of the springs. The various units are connected to one another by additional springs. In operation the springs and weights are adjusted to values which represent the coefficients of the secular equation to be solved, the whole device is driven by an eccentric of variable speed, and the frequencies of resonance, representing the roots of the equation, are measured.

KETTERING, Shutes and Andrews[1] introduced the method of analyzing the vibrational spectra of polyatomic molecules by the use of vibrating models consisting of steel balls representing the atoms, connected by springs representing the valence bonds. By vibrating such a model with a motor and eccentric system, the frequencies of resonance of the model can be picked up and measured. Despite the many advantages which this method possesses, it also has certain limitations. It is difficult, for example, to construct a model sufficiently close to the ideal of point masses and weightless springs, especially since the springs must be rigidly attached to the balls and must be capable of resisting tension, compression, bending, and in some cases torsion. For each of these multiple duties the spring must have the proper force constant. The most serious limitation, however, is the lack of flexibility of the apparatus. A model must be built, not only for each molecule, but also for each set of trial values of the various force constants, since the springs are not adjustable. Furthermore, there are many types of potential function which cannot be reproduced by such a model because of geometrical limitations—springs may get in one another's way, for example.

Because of the great power of the Andrews' method, it seemed important to devise a mechanical analyzer that would preserve the advantages and overcome the difficulties mentioned above. In order to achieve this end, the geometrical analogy between the molecule and the model was discarded, since what is really desired is a mechanical system having the same potential and kinetic energies (except for a scale factor) as the molecule. A set of coupled harmonic oscillators forms such a system if the coupling is of the proper form.

[1] Kettering, Shutes and Andrews, Phys. Rev. **36**, 531 (1930); F. Trenkler, Physik. Zeits. **36**, 162 (1935), etc.