ago, Moffitt[19] pointed out that the 18-kcal. discrepancy between $\Delta E_{at}(H_2O)$ and $2\Delta E_{at}(OH)$ is reduced if one properly accounts for promotional energies. First it was assumed that the energy of atomization can be separated into bond energies and promotional energies

$$\Delta E_{at}(H_2O) = 232 \text{ kcal.} = 2B_{OH} - P_{HOH} \qquad (43)$$
$$\Delta E_{at}(OH) = 107 \text{ kcal.} = B_{OH} - P_{OH}$$

But $P_{HOH} = P_{OH} = 11$ kcal. for the simple valence-bond structures $\Psi_1$ and $\Psi_1^{OH}$ (eq. 35 and 38). Therefore

$$\Delta E_{at}(H_2O) = 2\Delta E_{at}(OH) + P_{OH}$$
$$= 214 \text{ kcal.} + 11 \text{ kcal.} = 225 \text{ kcal.} \quad (44)$$

The 7-kcal. difference remaining is then attributed to hybridization, ionic–covalent resonance, H–H interaction, etc.

(19) W. Moffitt, *Rept. Progr. Phys.*, **17**, 173 (1959).

The diatomics-in-molecules theory leads to a quantitative explanation for the difference in atomization energies of $H_2O$ and OH. It is seen that an important factor is the H–H interaction, which in fact contributes 11 kcal. to the binding in $H_2O$. The promotional energy for the oxygen atom is found to be almost twice as large in right-angled $H_2O$ as in OH.

Questions relating to hybridization and/or ionic character cannot be answered by the present treatment. Addition of canonical *ionic* structures for $H_2O$ to the starting set, necessitating valence-bond representations of OH ground and excited states more refined than eq. 38, would lead to explanations in terms of relative ionic characters. In any case, more detailed OH molecule descriptions will be necessary before the energy of $H_2O$ can be determined by diatomics-in-molecules theory as a function of bond angle. Work is now in progress along these lines.

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# A Method of Diatomics in Molecules. II. H₃ and H₃⁺ [1]

BY FRANK O. ELLISON, NORMAN T. HUFF, AND JASHBHAI C. PATEL

The diatomics-in-molecules theory described in the preceding paper[2] is used to calculate the potential energy surfaces for $H_3$ and $H_3^+$. The energy of atomization $\Delta E_{at}$ of linear symmetrical ($R_{HH} = 1.8$ bohrs) $H_3$ is calculated to be 96.60 kcal., which corresponds to a classical activation energy of 13 kcal. (experimental, $\sim 7.7$ kcal.). The molecule-ion $H_3^+$ is found to be most stable as an equilateral triangle, $\Delta E_{at} = 223.8$ kcal. The totally symmetrical $A_1'$ and doubly degenerate $E_1'$ vibrational wave numbers are determined to be 3450 and 2330 cm.$^{-1}$, respectively. The zero-point energy is thus 11.5 kcal. and $\Delta E_{at}^\circ = 212.3$ kcal. The reaction $H_2 + H_2^+ = H_3^+ + H$ is calculated to be exothermic by 48 kcal.; it is speculated that this result, as well as the atomization energies, may be about 10 kcal. too high.

## Introduction

In the preceding paper (hereafter referred to as paper I),[2] there was proposed an approximate theory designed primarily to predict molecular stabilities and to provide understanding of the deviations from strict additivity of bond energies. In this paper we use the theory to calculate the potential energy surfaces for $H_3$ and $H_3^+$, as well as the vibrational structure of the latter molecule-ion.

## The H₃ Molecule

**Theory.**—We begin with the conventional valence-bond structures for $H_3$, which may be written A–B C and A B–C, the associated wave functions being

$$\Psi_1 = |a\bar{b}c| - |\bar{a}bc|$$
$$\Psi_2 = |a\bar{b}c| - |ab\bar{c}| \qquad (1)$$

The $a$, $b$, and $c$ represent 1s orbitals located on the three centers; a bar over the orbital denotes $\beta$-spin, no bar means $\alpha$-spin. The wave functions are not normalized, even for infinite separation of the nuclei; experience has shown us that diatomics-in-molecules theory is easier to execute if functions are left nonnormalized.

The simplest valence-bond wave functions for $H_2$ are utilized; for example

$$\Psi_1^{AB} = |a\bar{b}| - |\bar{a}b|$$
$$\Psi_1^{AB} = |a\bar{b}| + |\bar{a}b| \qquad (2)$$
$$\Psi_2^{AB} = |ab|, \ \Psi_4^{AB} = |\bar{a}\bar{b}|$$

These represent the ground $^1\Sigma_g^+$ state and excited $^3\Sigma_u^+$ states, respectively; analogous expressions for $\Psi_s^{BC}$ and $\Psi_s^{AC}$ are also needed.

The diatomics-in-molecules theory will be illustrated by evaluating two of the necessary integrals, $H_{12}^{AB}$ and $H_{22}^{AB}$, where

(1) Supported in part by a grant from the National Science Foundation.
(2) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963).

$$H_{nm}^{PQ} = \int \Psi_n A_{PQ}^{(PQ)} H_{PQ} A_{PQ} A_{(PQ)} \psi_n d\tau \qquad (3)$$

First, we may write

$$\psi_2 = a_1\bar{b}_2c_3 - a_1b_2\bar{c}_3$$
$$A_{AB}A_{(AB)}\psi_2 = |a\bar{b}|c - |ab|\bar{c} \qquad (4)$$

Employing the inverse of eq. 2, we find that

$$A_{AB}A_{(AB)}\psi_2 = \frac{1}{2}(\Psi_1^{AB} + \Psi_2^{AB})c - \Psi_3^{AB}\bar{c} \qquad (5)$$

Application of the diatomic hamiltonian $H_{AB}$ yields

$$H_{AB}A_{AB}A_{(AB)}\psi_2 = [E_1^{AB}\Psi_1^{AB}c + E_2^{AB}(\Psi_2^{AB}c - 2\Psi_3^{AB}\bar{c})]/2 \qquad (6)$$

where $E_1^{AB}$ and $E_2^{AB}$ are the ground singlet and excited triplet eigenvalues for $H_2$, the internuclear distance of which corresponds to the distance $R_{AB}$ in $H_3$. We now use eq. 2 to transform back again to the determinantal function basis, and then apply the supplementary anti-symmetrizer $A_{AB}^{(AB)}$

$$\mathcal{H}_{AB}\psi_2 = [E_1^{AB}(|a\bar{b}c| - |\bar{a}bc|) + E_2^{AB}(|a\bar{b}c| + |\bar{a}bc| - 2|ab\bar{c}|)]/2 \qquad (7)$$

where $\mathcal{H}_{AB} = A_{AB}^{(AB)}H_{AB}A_{AB}A_{(AB)}$. Introducing eq. 1 gives

$$\mathcal{H}_{AB}\psi_2 = [E_1^{AB}\Psi_1 + E_2^{AB}(2\Psi_2 - \Psi_1)]/2 \qquad (8)$$

from which we find that

$$H_{12}^{AB} = [E_1^{AB}S_{11} + E_2^{AB}(2S_{12} - S_{11})]/2$$
$$H_{22}^{AB} = [E_1^{AB}S_{21} + E_2^{AB}(2S_{22} - S_{21})]/2 \qquad (9)$$

where $S_{nm} = \int \Psi_n \Psi_m d\tau$.

Similarly it can be shown that

$$\mathcal{H}_{AB}\psi_1 = E_1^{AB}\Psi_1$$
$$\mathcal{H}_{AC}\psi_1 = [E_1^{AC}(\Psi_1 - \Psi_2) + E_2^{AC}(\Psi_1 + \Psi_2)]/2$$
$$\mathcal{H}_{BC}\psi_1 = [E_1^{BC}\Psi_2 + E_2^{BC}(2\Psi_1 - \Psi_2)]/2 \qquad (10)$$
$$\mathcal{H}_{AC}\psi_2 = [E_1^{AC}(\Psi_2 - \Psi_1) + E_2^{AC}(\Psi_1 + \Psi_2)]/2$$
$$\mathcal{H}_{BC}\psi_2 = E_1^{BC}\Psi_2$$
$$\mathcal{H}_A\psi_n = \mathcal{H}_B\psi_n = \mathcal{H}_C\psi_n = E_H\Psi_n$$

Table I

Energies (Kcal.) of States of $H_2$ as Function of Internuclear Distance

| $R$ (bohr)[a] | $E_{HH}$ ($^1\Sigma_g{}^+$)[b] | $E_{HH}*$ ($^3\Sigma_u{}^+$)[c] | $R$ (bohr)[a] | $E_{HH}$ ($^1\Sigma_g{}^+$)[b] | $E_{HH}*$ ($^3\Sigma_u{}^+$)[c] |
|---|---|---|---|---|---|
| 1.0 | $-78.20$ | 244.99 | 3.6 | $-16.61$ | 7.61 |
| 1.2 | $-103.58$ | 178.55 | 3.8 | $-13.15$ | 6.00 |
| 1.4 | $-109.56$ | 136.11 | 4.0 | $-10.38$ | 4.38 |
| 1.6 | $-105.89$ | 105.19 | 4.2 | $-8.07$ | 3.23 |
| 1.8 | $-97.35$ | 83.74 | 4.4 | $-6.00$ | 2.31 |
| 2.0 | $-86.74$ | 65.52 | 4.6 | $-4.38$ | 1.61 |
| 2.2 | $-75.20$ | 49.14 | 4.8 | $-3.00$ | 1.15 |
| 2.4 | $-64.13$ | 35.76 | 5.0 | $-2.08$ | 0.92 |
| 2.6 | $-53.52$ | 26.76 | 5.2 | $-1.38$ | .69 |
| 2.8 | $-43.83$ | 20.53 | 5.4 | $-0.92$ | .46 |
| 3.0 | $-35.30$ | 16.38 | 5.6 | $-.46$ | .23 |
| 3.2 | $-27.91$ | 12.69 | 6.0 | $-.23$ | .02 |
| 3.4 | $-21.45$ | 9.46 | | | |

[a] 1 bohr = 0.5292 Å. [b] Data for $R$ less than 4.2 bohrs obtained from W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960); for $R$ greater than 3.5 bohrs from D. Steele, E. R. Lippincott, and J. T. Vanderslice, *ibid.*, **34**, 239 (1962); data joined by smooth curve from 3.5 to 4.4 bohrs. [c] Data for $R$ less than 3.5 bohrs obtained from W. Kolos and C. C. J. Roothaan, note b; for $R$ greater than 2.5 bohrs from J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950); data joined by smooth curve from 2.0 to 4.0 bohrs.

Since 1s orbitals only are being used in the AO-basis from which eq. 1 and 2 are built, the treatment is not restricted to linear configurations of $H_3$; the internuclear distances $R_{AB}$, $R_{AC}$, and $R_{BC}$ may be chosen independently, and the corresponding diatomic energies $E_s{}^{PQ}$ and overlap integrals $S_{PQ}$ employed.

The experimental energies of $H_2$ in its ground singlet and excited triplet states are listed in Table I.

**Results.**—In Table II we list the ground and excited $^2\Sigma^+$ state energies (relative to $H_2 + H$) for linear $H_3$. *Energies calculated with and without overlap differed from each other by less than 0.001 kcal.* Structure projections $\nu_n = c_n \Sigma c_m S_{nm}$ calculated with and without overlap differed from each other by less than 3% in all cases investigated; the $\nu_n$ listed in Table II are those calculated with overlap included. In Table III we list the ground $^2B_2$ state energies of triangular $H_3$ as calculated without overlap. For the *equilateral* triangle, the calculated energy of $H_3$ is entirely independent of overlap.

The classical activation energy for the reaction $H_2 + H$ is thus computed to be about 13 kcal., which may be contrasted with the experimental value $\sim$7.7 kcal.[3] The "binding energy" or energy of atomization $\Delta E_{at}$ corresponding to the latter is $109.56 - 7.7 = 101.9$ kcal. *Ab initio* calculations involving no empirical

Table II

Calculated Energies and Structure Projections for Ground and Excited States of Linear $H_3$[a]

| $R_{ab}$ | $R_{bc}$ 1.0 | | 1.2 | | 1.4 | | 1.6 | | 1.8 | | 2.0 | | 2.4 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 180.2 | 0.50 | | | | | | | | | | | | |
| | 351.2 | | | | | | | | | | | | | |
| 1.2 | 126.4 | 0.63 | 79.2 | 0.50 | | | | | | | | | | |
| | 308.3 | | 261.4 | | | | | | | | | | | |
| 1.4 | 93.8 | 0.71 | 53.7 | 0.60 | 33.7 | 0.50 | | | | | | | | |
| | 290.2 | | 240.0 | | 215.1 | | | | | | | | | |
| 1.6 | 73.8 | 0.77 | 38.8 | 0.68 | 23.4 | 0.60 | 16.0 | 0.50 | | | | | | |
| | 284.5 | | 231.2 | | 202.6 | | 186.4 | | | | | | | |
| 1.8 | 62.2 | 0.81 | 30.7 | 0.74 | 17.5 | 0.67 | 12.8 | 0.59 | 13.0 | 0.50 | | | | |
| | 286.7 | | 230.8 | | 199.2 | | 180.0 | | 170.8 | | | | | |
| 2.0 | 53.9 | 0.85 | 24.1 | 0.80 | 12.9 | 0.74 | 11.3 | 0.67 | 13.4 | 0.59 | 16.5 | 0.50 | | |
| | 291.7 | | 233.5 | | 199.4 | | 176.8 | | 159.9 | | 154.0 | | | |
| 2.4 | 40.4 | 0.92 | 13.5 | 0.90 | 5.6 | 0.87 | 6.7 | 0.82 | 12.6 | 0.78 | 19.8 | 0.71 | 32.3 | 0.50 |
| | 305.0 | | 243.1 | | 204.4 | | 177.2 | | 159.6 | | 146.0 | | 128.1 | |
| 2.8 | 35.6 | 0.96 | 9.2 | 0.94 | 2.3 | 0.93 | 5.0 | 0.91 | 12.5 | 0.88 | 21.8 | 0.84 | 40.5 | 0.71 |
| | 319.8 | | 256.0 | | 215.0 | | 186.4 | | 166.9 | | 150.8 | | 126.2 | |
| 3.2 | 33.7 | 0.98 | 7.9 | 0.97 | 1.6 | 0.96 | 5.0 | 0.95 | 13.2 | 0.93 | 23.4 | 0.91 | 44.4 | 0.84 |
| | 332.0 | | 267.1 | | 226.0 | | 196.3 | | 175.8 | | 158.5 | | 130.8 | |
| 3.6 | 32.8 | 0.99 | 7.3 | 0.98 | 1.3 | 0.98 | 4.9 | 0.97 | 13.3 | 0.96 | 23.6 | 0.95 | 45.8 | 0.92 |
| | 341.3 | | 275.8 | | 234.1 | | 203.7 | | 182.7 | | 165.0 | | 135.8 | |
| 4.0 | 32.1 | 0.99 | 6.7 | 0.99 | 0.6 | 0.99 | 4.2 | 0.99 | | | | | | |
| | 346.6 | | 280.6 | | 238.5 | | 207.9 | | | | | | | |
| 4.4 | 31.6 | 0.99 | 6.2 | 0.99 | | | | | | | | | | |
| | 350.0 | | 283.9 | | | | | | | | | | | |

[a] Each entry in the table consists of the ground state energy followed by the structure projection $\nu_2$ for the ground state ($\nu_1 = \nu_2 - 1$) on the same line with the excited state energy on the second line ($\nu_1$ for excited state $= \nu_2$ for ground state). Energies are given in kcal. relative to $H_2 + H$; $R_{ab}$ and $R_{bc}$ are listed in bohrs (1 bohr = 0.5292 Å.).

All integrals $H_{nm}{}^{PQ}$ may thus be obtained, and the matrix elements $H_{nm}$ calculated according to eq. 13–15 in paper I.

The overlap matrix elements are determined as

$$S_{11} = 2 + 2\bar{S}_{AB}{}^2 - \bar{S}_{AC}{}^2 - \bar{S}_{BC}{}^2 - 2\bar{S}_{AB}\bar{S}_{AC}\bar{S}_{BC}$$

$$S_{12} = S_{21} = 1 - 2\bar{S}_{AC}{}^2 + \bar{S}_{BC}{}^2 + \bar{S}_{AB}{}^2 - \bar{S}_{AB}\bar{S}_{AC}\bar{S}_{BC} \quad (11)$$

$$S_{22} = 2 + 2\bar{S}_{BC}{}^2 - \bar{S}_{AB}{}^2 - \bar{S}_{AC}{}^2 - 2\bar{S}_{AB}\bar{S}_{AC}\bar{S}_{BC}$$

where $\bar{S}_{PQ} = \int 1s_P 1s_Q dv = (1 + R_{PQ} + R_{PQ}{}^2/3) \exp (-R_{PQ})$. The calculation can be done also *without overlap*, in which case $S_{11} = S_{22} = 2$ and $S_{12} = S_{21} = 1$.

data give binding energies ranging from 68.3 (molecular orbital method using three 1s orbitals including configuration interaction)[4] to 80.3 kcal. (molecular orbital "open-shell" method using six 1s orbitals, two with different screening parameters on each atom, including interaction of up to 66 configurations).[5] Typical results for the classical activation energy ob-

(3) L. Farkas, *Z. physik. Chem.*, **B10**, 419 (1931); A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London), **A152**, 124 (1935).

(4) V. Griffing, J. L. Jackson, and B. J. Ransil, *J. Chem. Phys.*, **30**, 1066 (1959).

(5) S. F. Boys and I. Shavitt, *Nature*, **178**, 1207 (1956); I. Shavitt, *J. Chem. Phys.*, **31**, 1359 (1959).
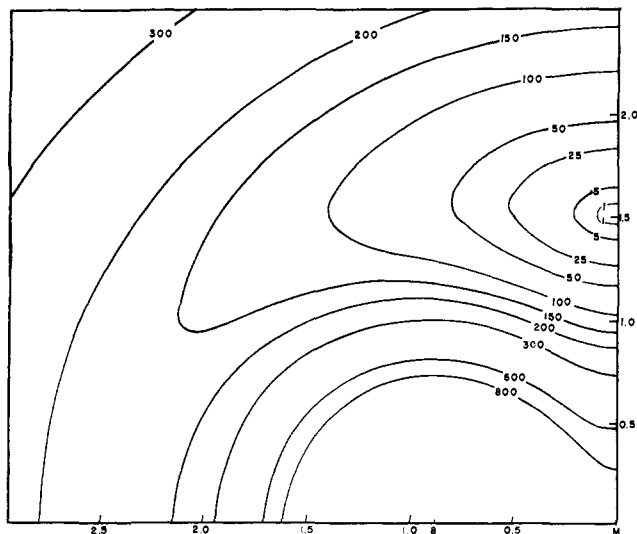
Fig. 1.—Energy of $H_3^+$ (in units of 0.01 e.v.) as a function of the position $x_A$, $y_A$ (in bohr units) of nucleus A relative to mid-point M of internuclear axis BC (one quadrant only of energy surface shown). $E(H_3^+) = 0$ for equilibrium equilateral triangle configuration. Locations of nucleus B and mid-point M of BC axis shown on abscissa ($R_{BC}$ held fixed at 1.76 bohr).

tained using semiempirical models are 14,[6] 8.76,[7] 7.5,[8] and 5.42 kcal.[9]

Of importance in the convergence investigation of diatomics-in-molecules theory will be a treatment of $H_3$ starting with a set of canonical structures enlarged to

TABLE III

CALCULATED ENERGIES FOR GROUND STATE OF TRIANGULAR $H_3^a$

| | $R_{ac}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1.2 | 1.4 | 1.6 | 1.8 | 2.0 | 2.4 | 2.8 | 3.2 |
| $R_{ab} = R_{bc}$ | | | | | | | | |
| 1.0 | 293.3 | 250.8 | 219.9 | 198.4 | 180.2 | | | |
| 1.2 | 222.0 | 179.5 | 148.6 | 127.2 | 108.9 | 79.2 | | |
| 1.4 | 155.3 | 149.3 | 118.4 | 96.9 | 78.7 | 49.0 | 33.7 | |
| 1.6 | 110.8 | 104.8 | 105.5 | 87.0 | 68.8 | 39.0 | 23.8 | 16.0 |
| 1.8 | 82.9 | 76.9 | 80.6 | 89.1 | 70.9 | 41.1 | 25.9 | 18.0 |
| 2.0 | 60.8 | 54.8 | 58.5 | 67.1 | 77.7 | 47.9 | 32.7 | 24.9 |
| 2.4 | 27.5 | 21.5 | 25.2 | 33.7 | 44.3 | 67.0 | 51.7 | 43.9 |
| 2.8 | 14.8 | 8.8 | 12.5 | 21.0 | 31.7 | 54.3 | 74.6 | 66.7 |
| 3.2 | 11.0 | 5.0 | 8.7 | 17.2 | 27.8 | 50.5 | 70.8 | 86.7 |
| 3.6 | 9.3 | 3.3 | 7.0 | 15.5 | 26.1 | 48.7 | 69.1 | 85.0 |
| 4.0 | 8.6 | 2.5 | 6.3 | 14.8 | 25.4 | 48.0 | 68.3 | 84.2 |
| 4.4 | 6.4 | 0.4 | 4.1 | 12.6 | 23.2 | 45.8 | 66.1 | 82.1 |
| 4.8 | 6.2 | .2 | 3.9 | 12.4 | 23.0 | 45.6 | 65.9 | 81.8 |
| 5.2 | 6.2 | .3 | 4.0 | 12.5 | 23.1 | 45.7 | 66.0 | 81.9 |
| 5.6 | 6.0 | .1 | 3.7 | 12.3 | 22.9 | 45.5 | 65.8 | 81.7 |
| 6.0 | 6.0 | .1 | 3.7 | 12.3 | 22.9 | 45.5 | 65.8 | 81.7 |

$^a$ Energies relative to $H_2 + H$ in kcal.; $R$ in bohrs.

include ionic structures and thus requiring valence-bond representations for $H_2$ more refined than eq. 2. Work is now in progress on this problem.

### The $H_3^+$ Molecule-Ion

**Theory.**—We assume that $H_3^+$ can be represented by a resonance of three independent structures represented by the valence-bond wave functions

$$\Psi_1 = |a\bar{b}| - |\bar{a}b|$$
$$\Psi_2 = |b\bar{c}| - |\bar{b}c| \qquad (12)$$
$$\Psi_3 = |a\bar{c}| - |\bar{a}c|$$

In the diatomics-in-molecules treatment, the total molecular hamiltonian $H$ is partitioned according to the assignment of electrons within the function $\Psi_m$ upon which $H$ operates in each integral $H_{nm}$ (see eq. 4

(6) H. Eyring, H. Gershinowitz, and C. E. Sun, *J. Chem. Phys.*, **3**, 785 (1935).

(7) V. Griffing and J. T. Vanderslice, *ibid.*, **23**, 1039 (1955).

(8) H. Eyring and E. M. Eyring, "Modern Chemical Kinetics," Reinhold Publishing Corp., New York, N. Y., 1963, p. 27.

(9) S. Sato, *J. Chem. Phys.*, **23**, 592 (1955).

and 5 in paper I and attendant text). Thus, when $H$ operates on $\Psi_1$, $\Psi_2$, and $\Psi_3$, it is written in the forms

$$H = H_{AB} + H_{ac} + H_{bc} - H_A - H_B$$
$$H = H_{BC} + H_{ab} + H_{ac} - H_B - H_C \qquad (13)$$
$$H = H_{AC} + H_{ab} + H_{bc} - H_A - H_C$$

respectively. We use capital letters AB, BC, and AC to designate hydrogen molecules, capitals A, B, and C for hydrogen atoms, and lower case ab, bc, and ac for hydrogen molecule-ions.

A simple valence-bond representation for the ground $^1\Sigma_g^+$ state of $H_2$ is employed, namely $\Psi_1^{AB}$ (the first of eq. 2) and similar expressions for $\Psi_1^{BC}$ and $\Psi_1^{AC}$. For $H_2^+$, the simple wave functions

$$\Psi_1^{ab} = (a + b)$$
$$\Psi_2^{ab} = (\bar{a} + \bar{b})$$
$$\Psi_3^{ab} = (a - b) \qquad (14)$$
$$\Psi_4^{ab} = (\bar{a} - \bar{b})$$

are used; the first two represent the ground $^2\Sigma_g^+$ states, and the second pair are for the excited $^2\Sigma_u^+$ states.

Application of eq. 18–27 in paper I yields the results

$$\mathcal{H}_{ac}\psi_1 = [E_1^{ac}(\Psi_1 + \Psi_2) + E_3^{ac}(\Psi_1 - \Psi_2)]/2$$
$$\mathcal{H}_{bc}\psi_1 = [E_1^{bc}(\Psi_1 + \Psi_3) + E_3^{bc}(\Psi_1 - \Psi_3)]/2$$
$$\mathcal{H}_{ac}\psi_2 = [E_1^{ac}(\Psi_1 + \Psi_2) + E_3^{ac}(\Psi_2 - \Psi_1)]/2$$
$$\mathcal{H}_{ab}\psi_2 = [E_1^{ab}(\Psi_2 + \Psi_3) + E_3^{ab}(\Psi_2 - \Psi_3)]/2 \qquad (15)$$
$$\mathcal{H}_{bc}\psi_3 = [E_1^{bc}(\Psi_1 + \Psi_3) + E_3^{bc}(\Psi_3 - \Psi_1)]/2$$
$$\mathcal{H}_{ab}\psi_3 = [E_1^{ab}(\Psi_2 + \Psi_3) + E_3^{ab}(\Psi_3 - \Psi_2)]/2$$
$$\mathcal{H}_{AB}\psi_1 = E_1^{AB}\Psi_1, \quad \mathcal{H}_{BC}\psi_2 = E_1^{BC}\Psi_2$$
$$\mathcal{H}_{AC}\psi_3 = E_1^{AC}\Psi_3$$

In these expressions, $E_1^{pq}$ and $E_3^{pq}$ are the ground and excited state energies of $H_2^+$, the internuclear distance of which corresponds to $R_{PQ}$ in $H_3^+$, and $E_1^{PQ}$ is the ground state energy of $H_2$ at an internuclear distance $R_{PQ}$. All integrals $H_{nm}$ can be obtained using these formulas as described in paper I.

The overlap matrix elements are

$$S_{11} = 2(1 + \bar{S}_{AB}^2)$$
$$S_{22} = 2(1 + \bar{S}_{BC}^2)$$
$$S_{33} = 2(1 + \bar{S}_{AC}^2)$$
$$S_{12} = 2(\bar{S}_{AC} + \bar{S}_{BC}\bar{S}_{AB}) \qquad (16)$$
$$S_{13} = 2(\bar{S}_{BC} + \bar{S}_{AC}\bar{S}_{AB})$$
$$S_{23} = 2(\bar{S}_{AB} + \bar{S}_{AC}\bar{S}_{BC})$$

Again, calculations are performed both with and without overlap ($\bar{S}_{PQ} = \int 1s_P 1s_Q dv$ and $\bar{S}_{PQ} = 0$, respectively).

The ground state energies of $H_2$ have already been listed in Table I. Best theoretical ground and excited state energies for $H_2^+$ obtained by Bates, *et al.*,[10] were employed in these calculations.

**Results.** — Diatomics-in-molecules theory predicts that $H_3^+$ is most stable in the equilateral triangle conformation, with $R_{HH} = 1.76$ bohrs. In Fig. 1 the potential energy surface for $R_{BC} = 1.76$ bohrs and variable $R_{AB}$ and $R_{AC}$ is displayed. The energy of atomization $\Delta E_{at}$ is computed to be 223.8 kcal. The fundamental vibrational wave numbers are computed to be $\omega_1(A') = 3450$ cm.$^{-1}$ and $\omega_2(E_1') = 2330$ cm.$^{-1}$ (see below) which yield 11.5 kcal. for the total zero-point energy, and thus $\Delta E_{at}^\circ = 212.3$ kcal. The reaction

$$H_2^+ + H_2 = H_3^+ + H \qquad (17)$$

is predicted to be exothermic: $\Delta E^\circ = -212.3 - (-61.1 - 103.2) = -48.0$ kcal. By an approximate

(10) D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc. (London)*, **246**, 215 (1953).

*ab initio* calculation on triangular $H_3^+$, Hirschfelder predicted that the reaction should be exothermic by more than 11 and probably by 38 kcal.[11] It is surmised, therefore, that diatomics-in-molecules theory in this approximation may give triangular $H_3^+$ about 10 kcal. more stability than it really has.

Linear $H_3^+$ is most stable ($\Delta E_{at} = 187.1$ kcal.) for $R_{AB} = R_{BC} = 1.6$ bohrs, but is unstable with respect to bending. Barker, Giddings, and Eyring[12] obtain $\Delta E_{at} = 158.09$ kcal. for linear $H_3^+$ in an *ab initio* calculation in which some integrals are approximated. If the variational energy error in the latter calculation is assumed equal to the energy error in the Wang calculation on $H_2$ (22 kcal.), $\Delta E_{at} \sim 180$ kcal. is indicated. Again, it appears that our result may be in error by about 10 kcal.

In its most stable configuration as an equilateral triangle, $H_3^+$ belongs to the group $D_{3h}$, and there exist one totally symmetrical ($A_1'$) vibration and one doubly degenerate vibration ($E_1'$).



$\nu_1(A_1')$　　　　$\nu_2(E_1')$　　　　$\nu_3(E_1')$
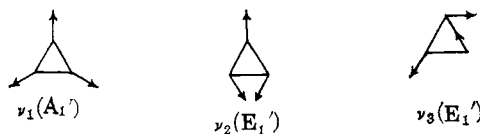
The potential and kinetic energies in the harmonic approximation may be written in the forms

$$2V = c_{11}S_1^2 + c_{22}(S_2^2 + S_3^2) \tag{18}$$

$$2T = d_{11}\dot{S}_1^2 + d_{22}(\dot{S}_2^2 + \dot{S}_3^2) \tag{19}$$

Taking atom A to be the upper vertex and lettering counterclockwise, one can show that[13]

$$x_A = S_3, \quad y_A = S_1 + S_2$$
$$x_{B,C} = (\mp 3^{1/2}S_1 \pm 3^{1/2}S_2 - S_3)/2 \tag{20}$$
$$y_{B,C} = (-S_1 - S_2 \mp 3^{1/2}S_3)/2$$

where $y$ is directed upward, $x$ to the right, and the upper sign refers to B, the lower sign to C. If one writes the kinetic energy in terms of cartesian coordinate velocities and then transforms to normal coordinates using eq. 20, it can be shown that $d_{11} = d_{22} = 3m_H$, from which it follows that the vibrational frequencies are given by $\nu_i = (c_{ii}/d_{ii})^{1/2}/(2\pi)$.

(11) J. O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938).

(12) R. S. Barker, J. C. Giddings, and H. Eyring, *ibid.*, **23**, 344 (1955).

(13) G. Herzberg, "Molecular Structure and Molecular Spectra," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 145–149.

Parabolas of the form $2V_i = a + bS_i + cS_i^2$ were fit to the total calculated energies of $H_3^+$ for slight displacements $S_i$ of the molecule from equilibrium. Results were as follows (in e.v. units of energy and bohr units of distance)

$$2V_1 = -73.806 - 0.007S_1 + 37.14S_1^2$$
$$2V_2 = -73.806 - 0.002S_2 + 16.83S_2^2 \tag{21}$$

In developing eq. 21, positive and negative displacements $S_i$ were decreased in regular steps until the coefficients $a$, $b$, and $c$ converged to the significant figures presented. The force constants were thus found to be 37.14 e.v./bohr² and 16.83 e.v./bohr², which yield $\omega_1 = \nu_1/c = 3450$ cm.⁻¹ and $\omega_2 = \omega_3 = \nu_2/c = 2330$ cm.⁻¹, where $c$ is the velocity of light.

As a check, the vibrational analysis was independently performed using the general expression

$$2V = 2V_0 + k_1(\Delta r_{ab}^2 + \Delta r_{bc}^2 + \Delta r_{ac}^2) +$$
$$k_2(\Delta r_{ab}\Delta r_{bc} + \Delta r_{ab}\Delta r_{ac} + \Delta r_{bc}\Delta r_{ac}) \tag{22}$$

The force constants were determined to be $k_1 = 2.21 \times 10^5$ dynes/cm. and $k_2 = 7.44 \times 10^3$ dynes/cm., from which one can determine

$$\omega_1 = [(3k_1 + 6k_2)/m_h]^{1/2}/(2\pi c) = 3450 \text{ cm.}^{-1}$$
$$\omega_2 = \omega_3 = [(3k_1 - 3k_2)/(2m_h)]^{1/2}/(2\pi c) = 2330 \text{ cm.}^{-1} \tag{23}$$

The central force field is obtained if we assume that $k_2 = 0$; this ultimately gives $\omega_1 = 3350$ cm.⁻¹ and $\omega_2 = \omega_3 = 2370$ cm.⁻¹.[14]

Energies for $H_3^+$ calculated with and without overlap differed from each other by less than 0.3 kcal. in all cases; results with and without overlap are identical for equilateral triangles.

The surmise was made above that our calculated energies for $H_3^+$ may be about 10 kcal. too low. The referee stated that he believes that this speculation is not well supported. Better would be a careful fundamental analysis of the origin of errors (eq. 2, 20, and 21 of paper I). Alternatively, the convergence might be investigated by enlarging the canonical set of structures (eq. 12) which in turn requires valence-bond representations for $H_2$ and $H_2^+$ more refined than eq. 2 and 14.

(14) Note Added in Proof (August 15, 1963).—In Table I of ref. 11, the total molecular energy results for $H_3^-$ obtained in an approximate *ab initio* calculation are listed. At the top of this table, the line "$R = 2.0a_0$, $R = 2.5a_0$, and $R = 3.0a_0$" should read "$\rho = 2.0a_0$, $= 2.5a_0$, and $= 3.0a_0$" (where $\rho = zR$). If the force constant $k_1$ is determined by fitting a parabola $V(R)$ to the corresponding three ground state energy results, one obtains $k_1 = 2.21 \times 10^{-5}$ dynes/cm., which agrees with our predicted value. The force constant and vibrational frequency calculations in the last section of ref. 11 are in error. Professor Hirschfelder has confirmed these observations in a private communication.