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Classical electrostatics were employed to study the configuration and potential energy of the (hypothetical) $(HF)_2$ molecule in the gaseous state. Of the planar models studied, a Z-shaped structure of C_{2h} symmetry with both $F-F-H$ angles equal to 32.5 degrees had a minimum potential energy.

I.

THE association of gaseous hydrogen fluoride has been studied by Briegleb[1] on the basis of an electrostatic model. Following the experimental work of Fredenhagen,[2] he assumes that associated molecules of the sort $(HF)_n$ exist in the vapor, where n is a small integer 2, 3···. In particular, he does not require that $n = 6$, as proposed by Hildebrand and others,[3] but assumes that varying amounts of $(HF)_2$, $(HF)_3$, etc. exist in equilibrium at any given temperature and pressure. This assumption has been given strong experimental support by Benesi and Smyth,[4] who report increased polarization of hydrogen fluoride gas upon increasing the applied pressure, indicating linear rather than ring polymers. Briegleb's calculation of the potential energy follows the classical method of Born and Heisenberg[5] in that he considers the potential energy to be the sum of Coulombic energy, repulsive energy, polarization energy, and dipole interaction. Dispersion of the dipole is taken into account. The hydrogen ion is assumed non-polarizable, while the effective polarizability α_{eff} of the fluoride ion is calculated from the expression:

$$\mu_{exp.} = er_0 - \alpha_{eff}e/r_0^2, \quad (1)$$

where $\mu_{exp.}$ is the dipole moment, e the electronic charge, and r_0 the interatomic distance in HF. For $r_0 = 1.007A$, $\alpha_{eff} = 0.595 \times 10^{-24}$. $\mu_{exp.}$ for HF was taken as 1.91 Debyes, as given by Hannay and Smyth.[6]

The potential energy of the $(HF)_2$ molecule as a function of the molecular configuration has been recomputed by the present authors. The notation used in describing the configuration of $(HF)_2$ is shown in Fig. 1. The HF distance r_{12} or r_{34} was taken as 1.007A, for reasons given in Part II of this paper. The $F-F$ distance r_{24} was taken as 2.58A as given by electron diffraction.[7] The angles φ_I and φ_{II} were taken as independent variables for determining the configuration. f_I and f_{II} were determined from the relation

$$f_I = \xi_1 + \xi_3 + \xi_4 \quad \text{and} \quad f_{II} = \gamma_1 + \gamma_2 + \gamma_3,$$

and the energy expression used was

$$\begin{aligned} U = &-e^2(1/r_{12} + 1/r_{34} + 1/r_{14} + 1/r_{23} \\ &- 1/r_{13} - 1/r_{24}) + B/r_{12}^7 + B/r_{34}^7 \\ &- \alpha_{eff}(f_I^2 + f_{II}^2) - (\alpha_{eff}^2 f_I f_{II}/r_{24}^3) \\ &\times [2\cos(180 - \varphi_I')\cos\varphi_{II}' \\ &\qquad - \sin(180 - \varphi_I')\sin\varphi_{II}']. \end{aligned} \quad (2)$$

The value of the repulsion constant B was determined from a similar energy expression for HF monomer:

$$U = -e^2/r + B/r^7 - \alpha_{eff}e^2/2r^4. \quad (3)$$

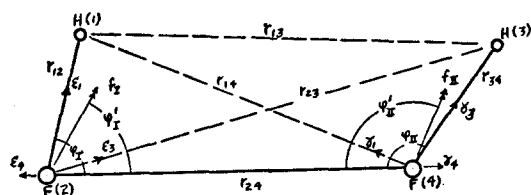Applying the condition $(\partial U/\partial r)_{r_0} = 0$, B can be

FIG. 1. Notation used in describing $(HF)_2$ molecule.

[1] G. Briegleb, Zeits. f. physik. Chemie B51, 9 (1941).
[2] K. Fredenhagen, Zeits f. anorg. allgem. Chemie 218, 161 (1934).
[3] Simons and Hildebrand, J. Am. Chem. Soc. 46, 2183 (1924); Long, Hildebrand, and Monell, J. Am. Chem. Soc. 65, 182 (1943).
[4] H. A. Benesi and C. P. Smyth, J. Chem. Phys. 15, 337 (1947).
[5] M. Born and W. Heisenberg, Zeits f. Physik 23, 388 (1924).
[6] Hannay and Smyth, J. Am. Chem. Soc. 68, 171 (1946).
[7] Bauer, Beach, and Simons, J. Am. Chem. Soc. 61, 19, (1939).

determined for $r_0 = 0.92A$, the interatomic distance in HF. This value of B was then used in Eq. (2) above.

Values of U from Eq. (2) are plotted as a function of φ_I and φ_{II} in Fig. 2. The potential minimum reported by Briegleb occurs on this energy surface at point A, where $\varphi_I = 0$, $\varphi_{II} = 67°$. (Briegleb, using $r_{12} = r_{34} = 0.92A$, found $\varphi_I = 0$, $\varphi_{II} = 83°$.) However, a lower minimum for the energy occurs at $\varphi_I = -\varphi_{II} = 32.5°$. (Point B, Fig. 2). This configuration has the advantage of higher symmetry, granting similar positions in the molecule to the identical protons (Fig. 3A).

For the symmetrical configuration (Fig. 3A) we find $W = 759.7$ kcal. for the reaction $2H^+ + 2F^- \rightarrow (HF)_2$. Data from Bichowsky and Rossini[8] give for the reaction

$$2H^+ + 2F^- \rightarrow 2HF, \quad W = 735.76 \text{ kcal.}$$
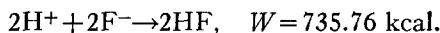
Thus for the reaction

$$2HF \rightarrow (HF)_2, \quad W = 23.9 \text{ kcal.}$$
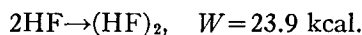
This value is in fairly good agreement with the value 28 ± 3 or 4 kcal., calculated from the shape of the $p-v$ isotherms of hydrogen fluoride.[9]

From the positive value for the energy change $2HF \rightarrow (HF)_2$ we see that $(HF)_2$ should be expected to be stable with respect to decomposition into 2HF.

The energy (11.9 kcal.) for one of the hydrogen bonds thus formed seems somewhat too high when compared with hydrogen bond energies of the type $O-H$ or $N-H$.[10] Unfortunately, the energy values computed by the present method are very sensitive to the interatomic distance (r_{12} or r_{34}) and this interatomic distance is not known for associated hydrogen fluoride.

II. ESTIMATION OF THE F–H DISTANCE IN (HF)₂

In general, the interatomic distance in a $H-X$ bond increases if the atom X forms a hydrogen bond with a second hydrogen. This increase in the $F-H$ distance caused by association was estimated from the infra-red spectrum of gaseous
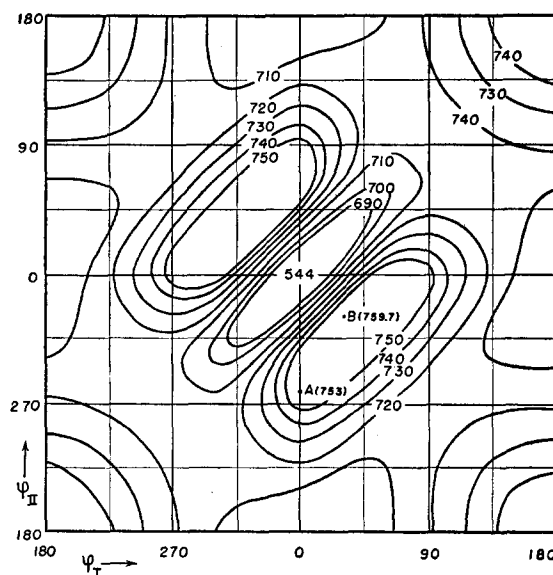

FIG. 2. Energy contour surface (in kcal./mole) based on electrostatic model. All energies shown are negative, relative to $2H^+ + 2F^- = 0$ kcal.

hydrogen fluoride given by Buswell, Maycock, and Rodebush.[11] The spectrum shows a weak absorption band with peaks at 2.59 and 2.47μ, assumed to be due to (HF), and a strong band with peaks at 2.85 and 2.97μ, assumed due to $(HF)_n$. Using the average value 2.91μ(3436
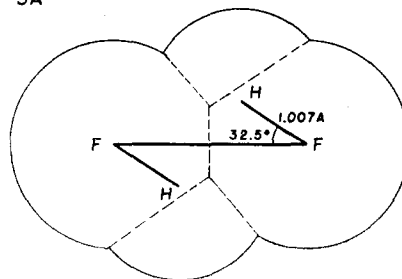
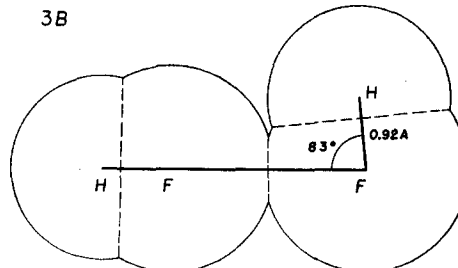FIG. 3(A). Proposed structure of (HF)₂ dimer.
(B) (HF)₂ structure proposed by Briegleb.

[8] Bichowsky and Rossini, *The Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).
[9] G. Briegleb, Naturwiss. **29**, 644 (1941).
[10] Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1942).
[11] Buswell, Maycock, and Rodebush, J. Chem. Phys. **8**, 362 (1940).

cm^{-1}) as the center of the $(HF)_n$ band, we can approximate ω_e as 3436 cm^{-1}. Employing the harmonic oscillator approximation,

$$k = 0.5863 \mu \omega_e^2$$

we find $k = 0.6627$ mgd/cm. Using Badger's rule in the form $k = 0.3003(R_e - 0.2385)^{-3}$,[12] we obtain $R_e = 1.007$A which is the value used for r_{12} and r_{34} in the calculations above. This value is within the limits set (1.0 ± 0.06) by Bauer et al. from electron diffraction.[7] A more precise value of the $F - H$ distance in $(HF)_2$ would be desirable. However, since only the configuration of $(HF)_2$ was of interest, and not its exact potential energy, the value of R_e as estimated above may be sufficiently accurate. It at least appears certain that the symmetrical configuration (Fig. 3A) is more stable than the unsymmetrical configuration (Fig. 3B); and that the reaction $2HF \rightarrow (HF)_2$ is exothermic.

A second attempt was made to determine the structure of the $(HF)_2$ molecule using the semi-empirical quantum mechanical method developed by Eyring et al.[13] for reaction rate studies. The energy E_i of each of the six bonds in $(HF)_2$ was determined from the Morse curves for HF, HH, and FF. We assume that the energy of any bond $E_i = A_i + \alpha_i$; where $A_i = \rho E_i$. A_i is the "Coulombic" part of the bond energy, ρ is a constant on the order of 0.10 to 0.20, and α_i is the

non-classical "exchange" portion of the bond energy. If we set $\alpha_1 + \alpha_2 = \alpha$; $\alpha_3 + \alpha_4 = \beta$, $\alpha_5 + \alpha_6 = \gamma$, $\Sigma A_i = Q$, then the total energy of the molecule is given by the London equation.[13]

$$E = Q - \{\tfrac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{\frac{1}{2}}. \quad (4)$$

Again we set $r_{12} = r_{34} = 1.007$A; $r_{24} = 2.58$A; and determine the energy E from Eq. (4), for different values of φ_I and φ_{II}. There is but one simple minimum in the energy surface corresponding to a linear molecule, with $\varphi_I = \varphi_{II} = 180°$, such that for $2H + 2F \rightarrow (HF)_2$, $W = 285.4$ kcal. From the Morse curve for HF we find $W = 295.8$ kcal. for $2H + 2F \rightarrow 2HF$. Comparison of these two values gives $W = -10.4$ kcal. for the reaction $2HF \rightarrow (HF)_2$, in poor agreement with the value $+23.9$ kcal. obtained for the same reaction by the electrostatic model. From the energy $W = 285.4$ kcal. for the reaction $2H + 2F \rightarrow (HF)_2$, we can compute the energy of the reaction $2H^+ + 2F^- \rightarrow (HF)_2$ from the equations: $2H \rightarrow 2H^+$, $2I = 624$ kcal.; $2F \rightarrow 2F^-$, $2E = 197$ kcal. Thus $W = 716.7$ for $2H^+ + 2F^- \rightarrow (HF)_2$ from the semi-empirical method, six percent lower than the value of 759.7 kcal. calculated by the electrostatic model. The fact that the semi-empirical quantum-mechanical method indicates a linear structure is probably not very significant, as it can be shown that this method indicates linear structures for three-atom systems which are known to be non-linear. (This minimizing of linear structures follows from the mathematical nature of the London equation itself.) The available data in the literature do not permit a complete quantum-mechanical treatment.

[12] George Glockler and George E. Evans, J. Chem. Phys. 10, 607 (1942).

[13] Glasstone, Laidler, and Eyring, The Theory of Rate Processes (McGraw-Hill Book Company, Inc., New York, 1941).