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Theoretical Studies of Proton-Transfer Reactions. I. Reactions of Hydride Ion with Hydrogen Fluoride and Hydrogen Molecules

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Abstract: Computations of the potential energy surfaces for the reactions of hydride ion with hydrogen molecule in the symmetrical reaction, and with hydrogen fluoride to produce hydrogen and fluoride ion, have been carried out by the LCAO–MO–SCF method using Gaussian basis functions. All integrals are analytically evaluated, and no approximations other than those inherent in the LCAO–MO–SCF method are used. The calculated energies are believed to be quite close to the Hartree–Fock limits. The reaction system H_3^- is found to have a potential energy surface qualitatively similar to that for the neutral H_3 system, and an activation energy for the hydrogen-exchange reaction of *ca.* 15 kcal/mole is calculated. The H_2F^- system has an unexpected potential energy surface in that no barrier is found along the minimum energy path between reactants and products. Instead, a minimum along the path is found indicating the existence of a stable H_2F^- complex with an energy *ca.* 8 kcal below that for the separated fluoride ion and hydrogen molecule.

Although *ab initio* LCAO–MO–SCF calculations for small molecules have been carried out for some time,[1,2] the difficulty of evaluating the multicenter integrals involving Slater-type orbitals (STO's) discouraged the widespread application to complex systems. The demonstration of the utility of Gaussian-type orbitals (GTO's) as basis functions for polyatomic systems[3] has recently led to studies on increasingly complex molecules, such as ethylene[4] and acetylene,[4,5] in which reasonable accuracy is attained. The use of GTO's allows the easy evaluation of all integrals, and it does not appear that the functions are markedly inferior to STO's for polyatomic systems.[6] Even with GTO's, however, the computations are extremely lengthy, since slightly less than N^4 integrals must be evaluated if N basis functions are used. For example, a calculation on methane using 48 GTO's[6] requires *ca.* 3 hr of computer time.

Probably because of the amount of computer time required, there has not been much work reported on computations of potential energy surfaces for reaction systems which involve many electrons. Considerable effort has been expended on computations for the H_3 system, however, since the system is simple and since it serves as a model for discussions of reaction rate theory. Johnston[7] has recently summarized the theoretical work in this area. It appears that H_3^- is the only more complex system to have been treated by nonempirical methods[8] prior to the present investigation. There are, of course, a variety of semiempirical methods for the construction of potential energy surfaces, and these have been widely applied. These latter methods, and their applications, have been adequately summarized in several recent texts.[7,9]

Quite recently, we have presented the results of a theoretical treatment of the proton transfer from hydrogen fluoride to hydride ion in preliminary form.[10]

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[1] R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1964.

[2] C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

[3] M. Krauss, *J. Chem. Phys.*, 38, 564 (1963).

[4] J. W. Moskowitz, *ibid.*, 43, 60 (1965).

[5] A. D. McLean, *ibid.*, 32, 1595 (1960).

[6] C. D. Ritchie and H. F. King, *ibid.*, 47, 564 (1967).

[7] H. S. Johnston, "Gas Phase Reaction Rate Theory," The Ronald Press Co., New York, N. Y., 1966, p 171 ff.

[8] V. Griffing and J. T. Vanderslice, *J. Chem. Phys.*, 23, 1039 (1955).

[9] K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 332 ff.

[10] C. D. Ritchie and H. F. King, *J. Am. Chem. Soc.*, 88, 1069 (1966).

All 12 electrons in the system were explicitly included, and the results are believed to be very close to the Hartree–Fock limits. The rather startling result obtained is that no barrier to reaction is found for the proton transfer.

Since our preliminary report, the results of an ambitious study of the potential energy surface for the reaction of ammonia with hydrogen chloride have been published.[11] Although the energies obtained in this latter study are quite far from the Hartree–Fock limits, it is worth noting that no barrier to reaction was found. Other qualitative features of the H_2F^- system were also found for this system.

In the present series of papers, we apply the LCAO–MO–SCF method, employing GTO's as basis functions, to the construction of potential energy surfaces for several simple proton-transfer reactions. Experimentally, proton-transfer reactions show a wide range of activation energies, and recent discussions of these reactions have required assumptions concerning the origins of the activation energies and the detailed shapes of the energy barriers.[12–14] Our study was initiated with the hope that some foundations could be provided for these assumptions. We believe now that the results bear on even more fundamental questions concerning rates of reactions.

In this first paper of the series, in which results for the H_3^- and H_2F^- systems are presented, it is worthwhile to review the approximations involved in the theoretical treatment, even though we shall have to return to these in connection with specific points for each individual system. Since the use of GTO's allows the analytical evaluation of all integrals, there are only two approximations in our treatment.

The first approximation arises from the incorrect description of electron correlation which is inherent in the SCF procedure itself. Early hopes[1] that correlation energies might remain constant for molecules containing the same number of electrons have been shattered by recent calculations.[15] The two ten-electron molecules, hydrogen fluoride and methane, for example, have estimated correlation energies[16] of 0.39 and 0.28 au, respectively. The difference of 0.11 au represents *ca.* 70 kcal/mole. It is comforting to note, however, that hydrogen molecule and hydride ion have correlation energies of 0.040 and 0.038 au, respectively; hydrogen fluoride and fluoride ion have values of 0.39 and 0.40 au; and water and hydroxide ion have values of 0.38 and 0.39 au, respectively.[16] Sinanoglu[15] has recently discussed the variations in correlation energies among similar molecules and has presented methods for estimating them.

The second approximation involved in our treatment arises from the approximation of the molecular orbitals by finite series expansions. In principle, Hartree–Fock calculations using larger and larger sets of Gaussian basis functions will converge to the true self-consistent-field (SCF) energy since these functions, in the limit, form a complete set. It was once feared that very long expansions would be required, since Gaussians have an analytically incorrect behavior for both the cusp at the nucleus and for the tail at large distances. In recent years, however, calculations by many people have shown that neither of these aspects is the source of serious difficulty in the case of Gaussian calculations for small molecules[3–6] and atoms.[17] For first-row elements the cusp is rather well represented by a linear combination of four or five Gaussians.[6] On the other hand, one might question whether or not molecular interaction energies are more sensitive to the tails of the orbitals than are the energies of the isolated molecules themselves. One can get a fairly good idea of what to expect for the asymptotic behavior of the most diffuse orbital by considering the region far from the center of an atom. There the radial component of the kinetic energy operator dominates the Hamiltonian with the result that the limiting radial dependence is the form $F(r) \exp [(-2\epsilon)^{1/2}r]$, where $F(r)$ is slowly varying compared with the exponential factor. There is bound to be a region of space where the Gaussian functions give too low an electron density. One would expect to find this region very roughly at the distance where the most diffuse Gaussian basis function has dropped off to half its maximum value. For the functions used here this corresponds to about three atomic units of distance (about 1.5 Å). The magnitudes of the orbitals are extremely low at this distance.[10] Indeed, detailed inspection of expressions for the variation of the SCF energy with respect to variations of the orbitals in this region of space indicate that the magnitudes of energy errors for potential energy surface calculations do not differ significantly from the corresponding errors for individual atoms. Numerical evidence concerning this point would be welcomed, but there already appears to be good cause for optimism.

In the present paper, we present the results of the computations of potential energy surfaces and electron densities for the H_3^- and H_2F^- systems. Some preliminary results on the H_2F^- system were reported earlier.[10]

Methods

Computational Programs. Three computer programs, all written in FORTRAN IV source language for the IBM 7044 computer, have been used in the present work. All programs use single precision of eight significant digits.

A program for the optimization of Gaussian exponents for single center systems is used as an aid in selecting basis sets. The nonlinear parameters are optimized by the method of steepest descents using derivatives approximated by finite differences. In practice, it is found that complete optimization of a set of functions is extremely difficult and time consuming because of the occurrence of multiple minima and flat regions of the multidimensional surface. Usually, some reasonable guess for initial functions, often taken from Huzinaga's compilations,[17] is made and these are partially optimized.[6]

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(11) E. Clementi, *J. Chem. Phys.*, **46**, 3851 (1967).

(12) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(13) Symposium on Proton Transfer Reactions, *Discussions Faraday Soc.*, **39** (1965).

(14) E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 317 (1965).

(15) C. Hollister and O. Sinanoglu, *J. Am. Chem. Soc.*, **88**, 13 (1966).

(16) See ref 6, and Table II of this paper, for the estimation of these quantities. Note that we take electron correlation energy to be the difference E(SCF) − E(exact, nonrelativistic), hence a positive quantity. Note also that reactions involving only closed-shell molecules differ qualitatively from those involving free radicals; see P. O. Lowdin, *Advan. Chem. Phys.*, **2**, 207 (1959); L. C. Snyder, *J. Chem. Phys.*, **46**, 3602 (1967).

(17) S. Huzinaga, *ibid.*, **42**, 1293 (1965).

The program for solution of the Hartree–Fock equations for polyatomic systems has been previously described.[6]

The third program used in this study takes the orbitals computed in the Hartree–Fock program and computes electron density contours which are plotted by a CalComp plotter on line with the IBM 7044 computer. Either electron density differences between two systems or total electron densities of one system can be plotted.

Choice of Basis Functions. The basis set used in the calculations on the H_3^- system was chosen by first optimizing five s-type GTO's for hydride ion. Using these five functions centered on each of the hydrogens, a partial optimization of p-type functions for the hydrogen molecule was then carried out. The final basis set obtained, consisting of five s-type and three p_x-type GTO's on each of the hydrogens, is summarized in Table I.

Table I. Gaussian Basis Set

Basis type	Exponent	Basis type	Exponent
	A. H_3^- System		
s	0.048797	p_x	0.200
	0.31396		0.800
	1.80969		6.00
	7.96074		
	32.2991		
	B. H_2F^- System:	Small Basis	
F s	0.720	H s	0.148
	3.60		0.6577
	18.00		4.2392
	90.00	F p	0.480
	450.0		2.40
			12.00
	C. H_2F^- System:	Large Basis	
F s	0.301	F p_x	0.208
	0.920		0.6206
	2.40		1.732
	8.00		4.788
	21.37		15.22
	60.70		65.66
	609.2	F p_y, p_z	0.190
	757.7		0.560
	3431.0		1.63
	23342.0		4.38
H s	0.10		14.2
	0.333		60.0
	1.00	H p_x, p_y, p_z	0.10
	3.60		0.50
	40.0		

It should be noted that the basis set is not optimum for the hydrogen molecule. It is hoped that a reasonable compromise has been obtained which gives good results for both hydride ion plus hydrogen molecule and other configurations of the H_3^- system. Although the s-type function with the smallest exponent is necessary to obtain a good energy value for the hydride ion, it causes some trouble for configurations of the H_3^- system in which all of the H–H distances become small, because of extensive overlap with other functions. When the overlap becomes very large, the coefficient of the function in the orthonormalized set becomes large, and serious round-off errors are produced in the Hartree–Fock matrix. In our calculations, the problem begins to show up for the linear symmetric configuration with H–H distances less than 1.7 au, and for equilateral triangular configurations when the H–H distances are less than *ca.* 2.5 au.

Because of the greater complexity of the H_2F^- system, accurate calculations require many more basis functions than for the H_3^- system. Since the time for a computation increases roughly with the fourth power of the number of basis functions used, it was decided to map the potential energy surface for the H_2F^- system with a small basis set and to carry out accurate calculations only for configurations along the minimum energy path on this surface.

The small basis set was taken directly from Harrison's paper[18] on the HF molecule (set B is used).

The large basis set was chosen from Huzinaga's compilation[17] and was partially optimized for the linear configuration of the H_2F^- system with $D(\text{F–H}) = 2.0$ au and $D(\text{H–H}) = 2.3$ au. The final basis sets used are summarized in Table I.

Results

H_3^- System. Using the basis sets shown in Table I, the calculated energy of the hydrogen molecule is -1.128 au, and that of hydride ion is -0.484 au. The Hartree–Fock limits of these species are -1.134 and -0.488 au, respectively, and the experimental energies are -1.174 and -0.526 au, respectively. A summary of the experimental, calculated, and Hartree–Fock energies of the various species encountered in the present study is shown in Table II.

Table II. Summary of Experimental and Calculated Energies[a]

Species	Basis[a]	$-E_{\text{calcd}}$	$-E_{\text{HF}}$[b]	$-E_{\text{nr}}$[c]
H^-	H_3^-	0.484	0.488[d]	0.526[d]
	H_2F^- (small)	0.434		
	H_2F^- (large)	0.468		
H_2	H_3^-	1.128	1.134[d]	1.174[d]
	H_2F^- (small)	1.122		
	H_2F^- (large)	1.131		
HF	H_2F^- (small)	99.403	100.07[e]	100.45[f]
	H_2F^- (large)	100.049		
F^-	H_2F^- (small)	98.697	99.46[g]	99.86[h]
	H_2F^- (large)	99.443		

[a] Basis sets used are those summarized in Table I. Energies are given in atomic units: 1 au = 27.201 ev = 627.2 kcal. [b] Estimated Hartree–Fock limits. [c] Nonrelativistic energy. This is the experimental value corrected for zero-point and relativistic energies. [d] Values reported by C. C. J. Roothaan and A. W. Weiss, *Rev. Mod. Phys.*, **32,** 194 (1960). [e] Value quoted in Table III of ref 15. [f] Experimental energy = -100.527 au (corrected for zero-point energy): B. J. Ransil, *Rev. Mod. Phys.*, **32,** 244 (1960); relativistic energy = 0.075 au: C. W. Scherr, J. N. Silverman, and F. A. Matsen, *Phys. Rev.*, **127,** 830 (1962). [g] E. Clementi, *J. Chem. Phys.*, **36,** 33 (1962); *IBM J. Res. Develop.*, **9,** 2 (1965). [h] Electron affinity of *F* = 0.129 au; nonrelativistic energy of *F* = -99.733 au: Scherr, *et al.*, footnote *f*.

Initial calculations on the H_3^- system were carried out for a linear symmetric geometry to locate the minimum energy distances for this configuration. A minimum energy of -1.5878 au is calculated for $D(H_1–H_2) = D(H_2–H_3) = 2.0$ au. Deviations from the symmetric configuration lead to decreases in the energy of the system, and, therefore, this point corresponds to a saddle point in the potential energy surface. The calculated energy at the saddle point is 0.024 au higher than that of the separated reactants.

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(18) M. C. Harrison, *J. Chem. Phys.*, **41,** 499 (1964).

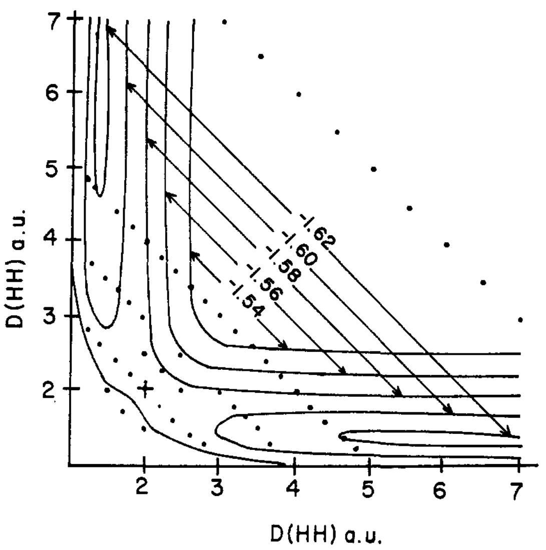

Figure 1. Energy contour diagram for the linear H_3^- system. Energy is given in atomic units. The points on the diagram represent actually calculated points from which the diagram was constructed by interpolation.

A series of calculations for various triangular configurations of the H_3^- system were then carried out. The results are summarized in Table III. It is found that the linear configuration represents the minimum energy space for the system. All other calculations were then carried out for approach of hydride ion along the H-H bond axis.

Table III. Energies for Various Configurations of the H_3^- Systems[a]

$D(H_1–H_2)$	$D(H_2–H_3)$	$D(H_1–H_3)$	$-E_{calcd}$, au
1.20	1.20	1.20	1.087^b
1.40	1.40	1.40	1.179^b
1.60	1.60	1.60	1.233^b
1.80	1.80	1.80	1.265^b
2.00	2.00	2.00	1.282^b
2.08	2.08	4.00	1.579
2.02	2.02	4.00	1.586
2.15	2.15	3.80	1.562
1.70	1.70	3.40	1.576
2.00	2.00	4.00	1.588
2.25	2.25	4.50	1.582
2.50	2.50	5.00	1.569
3.00	3.00	6.00	1.531
5.00	5.00	10.00	1.394

[a] All energies and distances are reported in atomic units. [b] For these calculations, the s-type basis functions with the exponent of 0.048797 were deleted from the basis set to avoid near redundancies. The calculations on the nonlinear configurations utilized p_x-, p_y-, and p_z-type functions with the exponents given in Table I for the p_z functions.

The contour diagram obtained for the linear system is shown in Figure 1, and a "reaction coordinate" diagram is shown in Figure 2. The contour diagram was constructed from the point-by-point computations as indicated on the diagram.

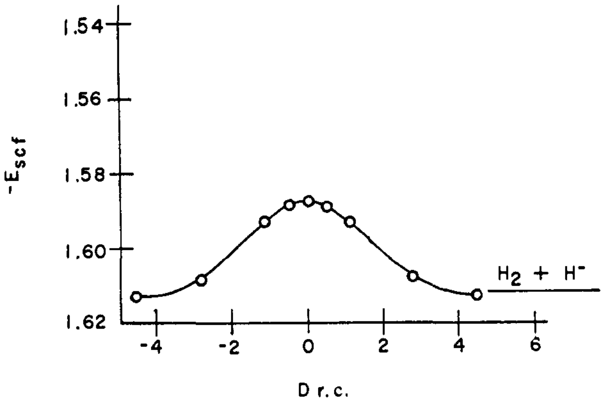

Figure 2. Energy as a function of distance along the minimum energy path for the H_3^- system. The distance is defined as $D_{rc} = (2)^{1/2}[D(H_1H_2) - D(H_2H_3)]$.

Electron density contour diagrams for several configurations of the H_3^- system along the minimum energy path of the surface shown in Figure 1 were computed. The changes in electron densities which occur along the reaction path are more clearly shown by the contour diagrams in which the electron densities of two hydride ions, one centered at each of the end hydrogens of the H_3^- system, are subtracted from the total system densities. Diagrams of this sort are shown in Figures 3–7. The diagrams represent the shifts in electron densities which occur when two hydride ions interact with each other and with a proton in between them.

The use of Koopman's theorem[19] allows us to construct a surface for the neutral H_3 system from our data for the H_3^- system. The results are shown in Figure 8. The linear symmetric H_3 system is found to have a minimum energy of -1.55 au at an optimum H-H distance of *ca.* 1.7 au. The separated reactants, $H_2 + H$, have a calculated energy of -1.57 au. An activation energy of 0.02 au is, therefore, obtained for this reaction.

H_2F^- System. The experimental energies, Hartree–Fock limits, and calculated energies for HF, F^-, H_2, and H^- are summarized in Table II. Results from both the small and large basis set computations are shown.

Several preliminary calculations, using the small basis set, were carried out for various geometries of the H_2F^- system. The results, summarized in Table IV, indicate that the linear configuration of the system is most favorable. All subsequent calculations were, therefore, carried out for approach of hydride ion along the H-F bond axis. The results of a series of calculations with the small basis set were used to construct the potential energy surface shown in Figure 9.

Table IV. Energies for Various Configurations of the H_2F^- System[a]

$D(F–H_1)$	$D(H_1–H_2)$	$D(F–H_2)$	$-E_{calcd}$
2.02	1.40	2.02	99.580
2.06	1.60	2.06	99.606
2.12	1.40	2.12	99.617
2.10	1.40	3.50	99.872
2.00	1.50	3.50	99.877
2.20	1.50	3.70	99.888
1.90	1.80	3.70	99.893
18.60	1.40	20.00	99.819
1.74	18.26	20.00	99.840

[a] The small basis set of Table I was used for all calculations. Energies and distances are in atomic units.

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(19) See ref 1, p 32.

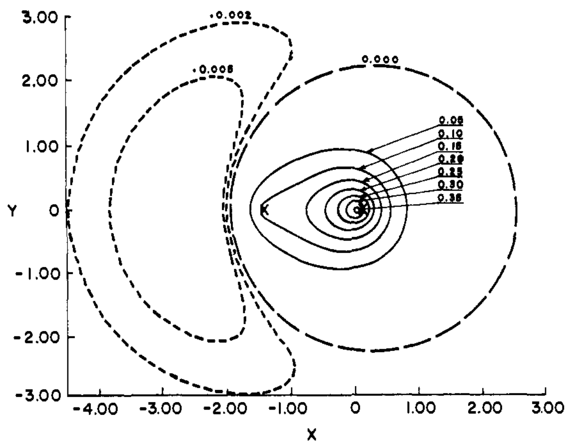

Figure 3. Electron density difference diagram for the linear H_3^- system at various points along the minimum energy path. The locations of nuclei are given by X's. The central hydrogen nucleus is located at $x = 0$, $y = 0$. The electron densities of two hydride ions, one superimposed on the left-most hydrogen and the other on the right-most hydrogen, are subtracted from the total electron density of the H_3^- system. $D_{rc} = 9.92$, where D_{rc} is defined as in Figure 2.

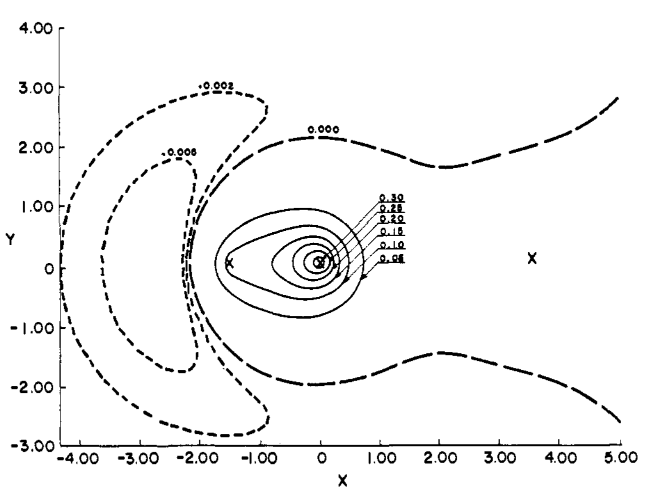

Figure 4. Electron density difference diagram (see caption to Figure 3); $D_{rc} = 2.84$.

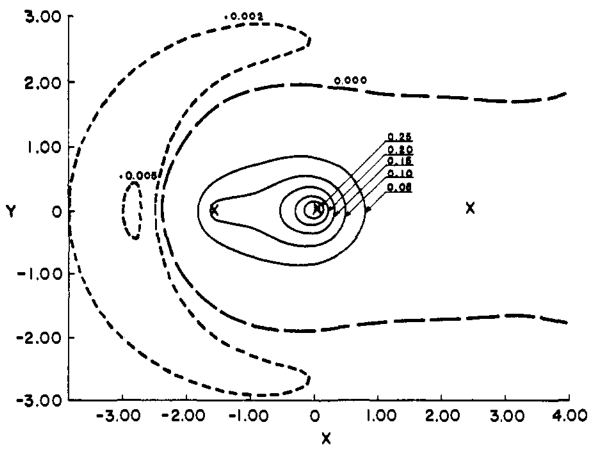

Figure 5. Electron density difference diagram (see caption to Figure 3); $D_{rc} = 1.03$.

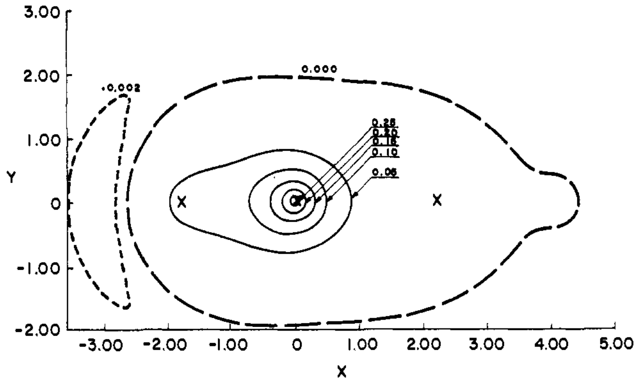

Figure 6. Electron density difference diagram (see caption to Figure 3); $D_{rc} = 0.53$.

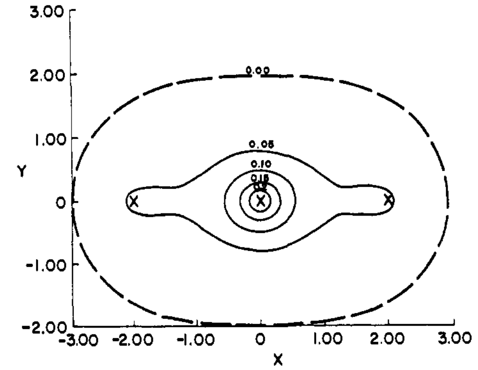

Figure 7. Electron density difference diagram (see caption to Figure 3); $D_{ro} = 0$.

The large basis set was then used to compute energies for various points along the minimum energy path of this surface. Occasional points off the minimum energy path were computed to be sure that the path was being reproduced by the more accurate calculations. The results of these calculations are summarized in Table V, and a "reaction coordinate" diagram is shown in Figure 10.

Table V. Calculated Energies for the Linear H_2F^- System[a]

$D(F\text{–}H_1)$	$D(H_1\text{–}H_2)$	$-E_{calcd}$
1.74	∞	100.517
1.85	3.00	109.569
1.95	2.35	100.574
1.80	2.20	100.567[b]
2.20	2.10	100.574[b]
2.20	1.90	100.575
2.40	1.80	100.577
2.70	1.60	100.582
2.70	1.40	100.577[b]
3.00	1.80	100.577[b]
3.10	1.50	100.585
3.60	1.45	100.586
∞	1.40	100.574

[a] Calculations employing the large basis set of Table I. All energies and distances are in atomic units. [b] These points are off the minimum energy path shown in Figure 9.

Although the minimum energy path found with the small basis is reproduced quite well with the extended basis set, the relative energies along the path are quite different. With the small basis set, a minimum point along the path is found at $D(F\text{–}H) \cong 2.2$ and $D(H\text{–}H) \cong 2.0$ au, which is *ca.* 44 kcal below the energy of the separated products of the reaction. With the large basis set, a minimum is found at $D(F\text{–}H) \cong 3.6$ and $D(H\text{–}H) \cong 1.45$ au, with an energy only *ca.* 8 kcal below that of the products of the reaction.

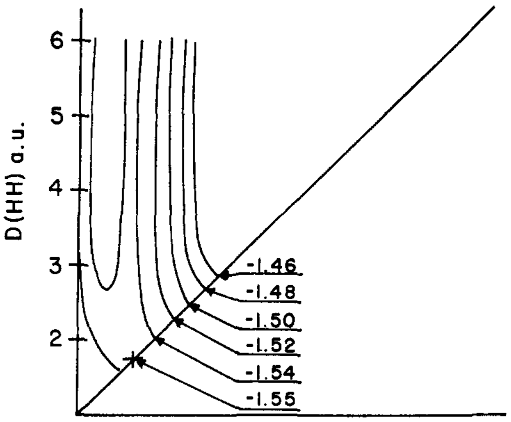

Figure 8. Energy contour diagram for the linear H_3 system. Energy is given in atomic units.

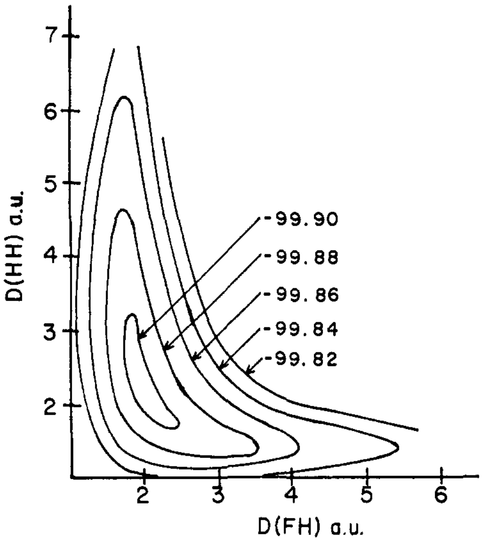

Figure 9. Energy contour diagram for the linear H_2F^- system. Energy is given in atomic units. All results are from the small basis set computations.

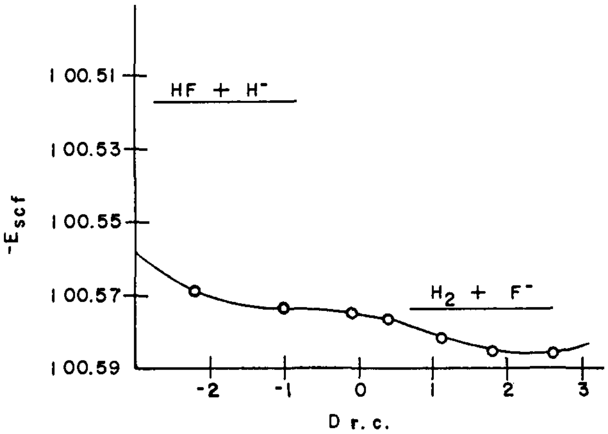

Figure 10. Energy as a function of distance along the minimum energy path for the H_2F^- system distance is defined as $D_{rc} = (2)^{1/2}[D(FH) - D_0(FH) - D(HH) + D_0(H_2)]$. Results are from the large basis set computations.

Both basis sets show the complete absence of a barrier along the minimum energy path between reactants and products.

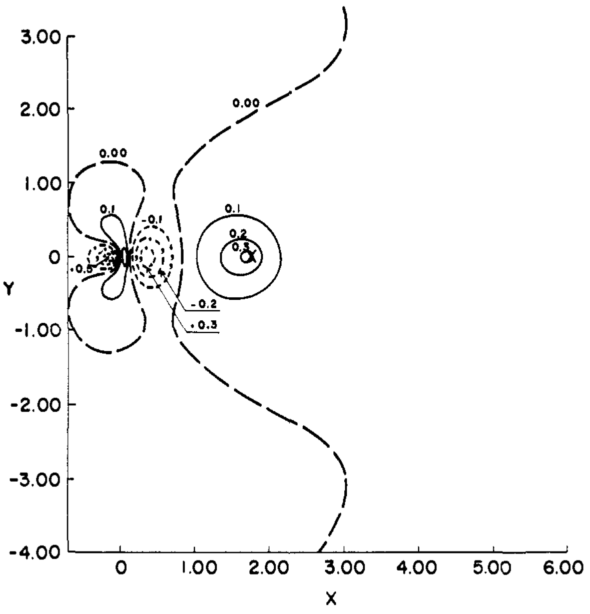

Figure 11. Electron density difference contour diagram for the linear H_2F^- system at various points along the minimum energy path. The locations of nuclei are marked by X's. The central hydrogen nucleus is located at $x = 0, y = 0$. The electron densities of fluoride ion superimposed on the fluorine nucleus and of hydride ion superimposed on the right-most hydrogen nucleus are subtracted from the total electron density of the H_2F^- system. All results are from the large basis set computations. $D_{rc} = -\infty$, where D_{rc} is defined as in Figure 10.

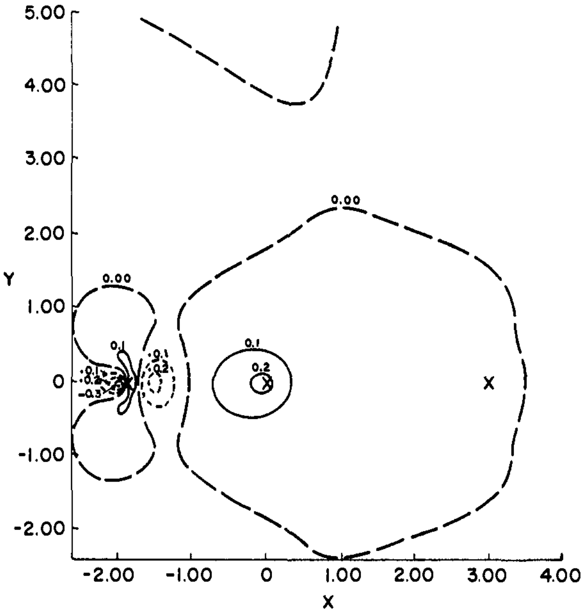

Figure 12. Electron density difference contour diagram (see caption to Figure 11); $D_{rc} = -2.12$.

Electron density contour diagrams were constructed for several configurations of the system from the large basis set calculations. The diagrams shown in Figures 11–15 are electron density difference contours similar to those for the H_3^- system. From the electron density of the H_2F^- system, in the given configuration, are subtracted the fluoride ion and hydride ion electron densities. The diagrams, therefore, show the shifts in electron density which occur when fluoride and hydride

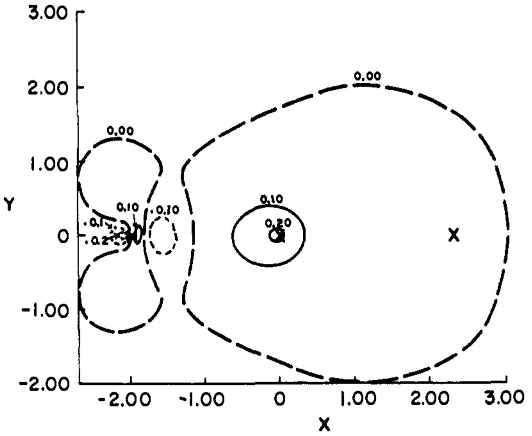

Figure 13. Electron density difference contour diagram (see caption to Figure 11); $D_{rc} = -1.06$.

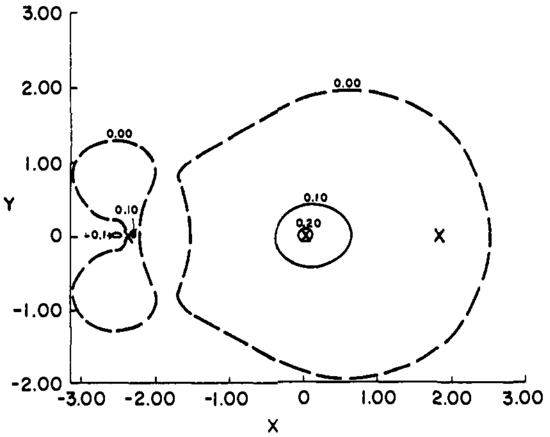

Figure 14. Electron density difference contour diagram (see caption to Figure 11); $D_{rc} = +0.51$.

ions interact with each other and with a proton in between them.

Discussion

The present results may be compared to the early results of Griffing and Vanderslice[8] for the H_3^- system. These authors used a minimal STO basis set with optimized exponent and calculated energies for the linear symmetrical configuration of the system. A minimum energy of -1.512 au was obtained for D(H-H) = 2.2 au. By application of Koopman's theorem, they also obtained an optimum energy for the linear symmetric H_3 system of -1.532 au for D(H-H) = 2.1 au and calculated an activation energy of 46 kcal for this reaction. The experimental value for the activation energy is *ca.* 8 kcal for the H_3 system and is not known for the H_3^- system. Our calculated value of *ca.* 12 kcal for the activation energy, and a minimum energy linear symmetric configuration with D(H-H) $\cong$ 1.7 au for the neutral system, is in fair agreement with the experimental value and with the accurate calculations carried out by Conroy.[20] This latter study gave an activation energy of *ca.* 7 kcal and an optimal linear symmetric configuration with D(H-H) = 1.72 au. Our present calculations have not been carried out for small enough grids on the surface to check the existence of the shallow minimum found by Conroy.

Interpretation of the experimental results of a study of the scattering of hydride ion by hydrogen molecules indicates a repulsive potential, and the data are best fitted by the empirical equation, $V(R) = 24.6 \exp(-2.18R)$ ev, with R expressed in angstrom units.[21] If we take R as the distance between one of the end hydrogen nuclei and the center of the other H-H bond distance at the saddle point on our surface, $R = 3.0$ au or 1.59 Å, and a repulsive potential of 0.76 ev or 0.028 au is calculated from this equation. The saddle point in the surface shown in Figure 1 is 0.024 au above the calculated energy of the separated hydride ion and hydrogen molecule. The agreement of our calculated value and that from the empirical equation indicates that the surface is not unrealistic.

The potential energy surface for the H_2F^- system is remarkable in its dissimilarity to those of the H_3^- and H_3 systems. There is no indication of a barrier in the surface computed with the small basis set, and this feature is verified in the large basis set calculations. Both calculations show an attractive potential between the hydride ion and HF molecule and between the fluoride ion and hydrogen molecule for all reasonable distances of approach. It is unfortunate that we have no experimental data for this system. The thermochemical data (Table II) show the reaction of hydride ion with hydrogen fluoride to be exothermic by 0.044 au (actually the value is for $\Delta E_0°$ corrected for zero-point energies), and the large basis set calculation gives a value of 0.057 au. There is no reason to suspect that this good agreement will not extend to the rest of the surface calculated with the large basis set.

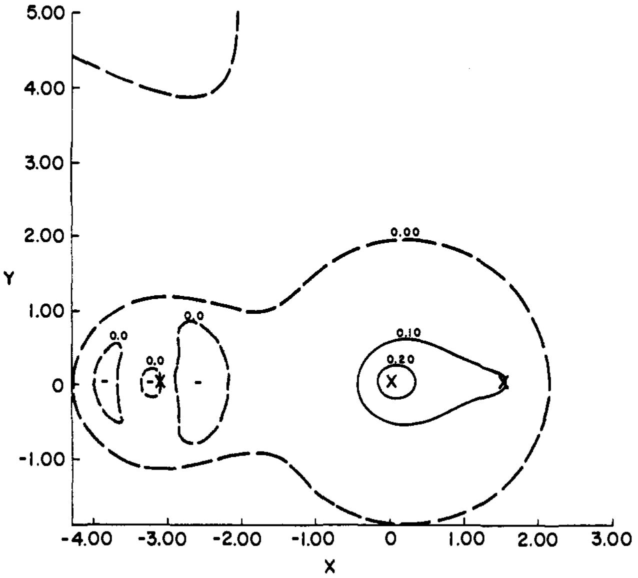

Figure 15. Electron density difference contour diagram (see caption to Figure 11); $D_{rc} = +1.78$.

The reliability of the potential energy surfaces computed in the present work can be questioned on the basis of the two approximations mentioned in the introductory section of this paper.

In the small basis set calculations for the H_2F^- system, considerable distortion of the surface arises from the limited basis set. Since the bases were optimized for the HF molecule,[18] it is not surprising that the energies calculated for the fluoride ion plus hy-

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(20) H. Conroy and B. L. Bruner, *J. Chem. Phys.*, 42, 4047 (1965).
(21) E. A. Mason and J. T. Vanderslice, *ibid.*, 28, 1070 (1958).

drogen molecule are higher than those for the HF molecule plus hydride ion. The wave functions for the anions are considerably more diffuse than those for the molecules, as can be seen in the electron density diagrams of Figures 3 and 11.

The poor energy obtained for fluoride ion, relative to hydrogen fluoride, is primarily responsible for the distorted potential energy surface which is obtained with the small basis set. As mentioned above, the thermochemical data for the H_2F^- system show that the reaction of hydride ion with hydrogen fluoride is exothermic by 0.044 au. The small basis set calculations give an energy of +0.018 au for the reaction. The minimum energy point in the surface is calculated to have an energy 0.069 au below that of separated hydrogen fluoride and hydride ion, and 0.087 au below that of separated hydrogen and fluoride ion. The large basis set calculations show a minimum energy point in the surface which is 0.069 au below the energy of hydrogen fluoride and hydride ion, but only 0.011 au below that of separated hydrogen and fluoride ion. The improvement in calculated energy on going from the small basis set to the large basis set is nearly constant at 0.68 au for configurations of the linear system ranging from $D(\text{FH}) = 1.74$, $D(\text{HH}) = \infty$ to $D(\text{FH}) = 2.70$, $D(\text{HH}) = 1.60$, and then increases for points further along the reaction coordinate to the value of 0.75 au for the separated products. The improvement in energy is a nearly monotonic function of the distance along the minimum energy path.

One other source of distortion of the surface arising from limited basis sets was considered. It seemed conceivable that close approach of hydride ion to the hydrogen fluoride molecule, or approach of hydrogen molecule to fluoride ion, might allow the limited basis sets to be shared in some way that would lead to the low energies for the intermediate configurations of the system. Even though the facts given in the preceding paragraph indicate that this is improbable, we have specifically checked the point by carrying out calculations in which off-centered functions are used. Calculations for both hydride ion and for hydrogen fluoride were made in which the full H_2F^- basis sets were used, with some of the basis functions off-center at the points corresponding to the locations of the absent nuclei. These calculations gave values for the energies of both species which were only negligibly lower than those calculated without the use of the off-center functions.

For the reasons given above, it appears unlikely that the inclusion of more basis functions could alter the results of the relative energies calculated with the large basis set.

The effect of inclusion of electron correlation energies is extremely difficult to estimate. There can certainly be no doubt that a considerable distortion of the surfaces in the regions of complete dissociation into atomic and ionic fragments might result from this source. It appears, however, that correlation energies are not sensitive to changes in bond distances over moderate ranges near the equilibrium separations in molecules.[15] It has been reported,[22] for example, that the correlation energy of hydrogen molecule remains constant for $R(\text{H–H})$ ranging from zero to the equilibrium separation.

Sinanoglu[15] has suggested two primary sources of changes in correlation energies on forming molecules from the neutral atoms. The first of these involves changes in the occupation of the atomic-like orbitals, and the second involves the occurrence of low-lying unoccupied MO's in the molecules formed. For our cases, the first effect is very difficult to estimate, but it appears that the second is unimportant. For the H_2F^- system, for example, the energy difference between the highest occupied and the lowest unoccupied orbitals has a maximum range from 0.481 to 0.542 au for the geometries reported in Table V. Not only is this difference not very sensitive to the geometry of the complex, but it is large enough in all cases that one does not expect appreciable configuration interaction.

We may very well suspect that inclusion of electron correlation, if it changes things at all, will lower the energies of the intermediate configurations relative to the separated species. The suspicion is based on the fact that going to intermediate configurations involves the formation of a twelve-electron species from a ten- and a two-electron species in the case of the H_2F^- system, which, therefore, increases the number of pair interactions.[15] This effect is responsible for the attraction of two helium atoms, for example, at moderate distances of approach and, more generally, for the attractive part of the van der Waals potential arising from London forces.

Having convinced at least ourselves that the present results are meaningful, it is now interesting to examine the electron density shifts that occur in the two systems during reaction. The electron density contour diagrams shown in Figures 3–7 and 11–15 exhibit several remarkable features. In particular, the entirely different natures of the electron density shifts for the H_3^- and H_2F^- systems are notable and emphasize the different natures of the potential energy surfaces for the two different systems.

The diagram in Figure 3, essentially shows the shift in electron density that occurs on protonating hydride ion. The expected contraction of the wave function and buildup of density around the proton and in the bonding region are apparent. The approach of hydride ion to the hydrogen molecule results in an even greater contraction of the wave function in directions both parallel and perpendicular to the bond axis and causes a decrease in the electron density at the central proton, probably because of simple polarization effects. The electron density at the transition state looks peculiarly bonding in that there is a buildup of electron density in the regions between both end hydrogens and the central proton.

Some of the general features of the H_3^- system electron densities are also observed for the H_2F^- system. The contraction of the wave function and the decrease in electron density around the central proton as the ion and molecule approach one another are seen for both systems.

The differences of the two systems are, however, much more striking. Figure 11 shows the shift in electron density which occurs on protonating fluoride ion. As expected, there is a general contraction of the wave function about the fluorine nucleus and a buildup of density at the proton. Surprisingly, there is a *decrease* in the electron density in the bond region and on the

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(22) W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, 32, 219 (1960).

back side of the fluorine nucleus.[23] Separate contour diagrams for the σ- and π-electron systems of hydrogen fluoride molecule show that the π system simply undergoes a general contraction from that in fluoride ion, and that nearly all of the detailed shifts shown in Figure 11 occur in the σ system. The diagrams suggest that there is a large amount of charge transfer from a p,σ orbital of fluoride to the s orbital of the hydrogen. The charge transfer from fluorine to hydrogen molecule is indicated even for rather large distances as shown in Figure 15. Similar types of electron density shifts are found in the reactions of other first-row hydrides with hydride ion, as will be reported in separate papers, and it appears that the charge transfer observed for the H_2F^- system is fairly general.

It will also be shown in the following papers that the potential energy surface for the H_2F^- system is typical of those for several proton-transfer reactions and that the well-known potential energy surface characteristic of the H_3^- and H_3 systems is atypical.

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[23] This behavior may be contrasted to the shifts of electron densities which occur when two neutral atoms form a molecule. See, for example, P. R. Smith and J. W. Richardson, *J. Phys. Chem.*, **69**, 3346 (1965); R. F. W. Bader and W. H. Henneker, *J. Am. Chem. Soc.*, **88**, 280 (1966).

Theoretical Studies of Proton-Transfer Reactions. II. The Reaction of Water with Hydride Ion

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Abstract: The results of computation of the potential energy surface for the reaction of water with hydride ion are described. The LCAO–MO–SCF method, using Gaussian basis functions, with all integrals analytically evaluated has been used, and the final calculations are believed to be quite close to the Hartree–Fock limits. The computations show the absence of a classical activation barrier for the reaction. The theoretical results are compared with experimental data which have been reported in the literature, and it is found not only that the results are consistent, but that the theoretical results provide an explanation of otherwise puzzling isotope effects on the solution reaction. Attention is called to the role of solvent in providing activation energies for proton-transfer reactions in solution.

In the preceding paper of this series,[1] we described the computations of potential energy surfaces for the reactions of hydride ion with hydrogen molecule and with hydrogen fluoride. The theoretical results, which are completely nonempirical, were shown to be consistent with the limited amount of experimental data available for the systems. The most interesting part of the results, the absence of an activation barrier in the reaction of hydrogen fluoride with hydride ion, could not be substantiated because of the absence of experimental data for that system.

In the present paper, we report the results of *ab initio* LCAO–MO–SCF calculations of the potential energy surface for the reaction of water molecule with hydride ion to produce hydroxide ion and hydrogen molecule. In this case, experimental data concerning the reaction in both gas and solution phases have been reported.[2–4]

Methods and Results

Descriptions of the computer programs used and of the method of choosing basis sets for the computations have previously appeared.[1,5] In the present study, as in that of the H_2F^- system,[1] the potential energy surface was mapped using a limited basis set, and final calculations with an extensive basis set were carried out for points along the minimum energy path on the surface. Only enough points off the minimum energy path were examined with the large basis calculations to be sure that the path was being reproduced.

Both the small and large basis sets used are those presented in a previous paper.[5] The basis functions centered on the hydride ion are identical with those centered on the water protons.

The experimental energies, estimated Hartree–Fock limits, and energies calculated with both small and large basis sets for the various species involved in the reaction studied are shown in Table I.

A series of initial calculations with the small basis set were carried out to determine the optimum direction of approach of hydride ion to water molecule, and of

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[1] C. D. Ritchie and H. F. King, *J. Am. Chem. Soc.*, **90**, 825 (1968).

[2] J. F. Paulson, "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, Chapter 3.

[3] W. K. Wilmarth, J. C. Dayton, and J. M. Fluornoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953).

[4] J. M. Fluornoy and W. K. Wilmarth, *ibid.*, **83**, 2257 (1961).

[5] C. D. Ritchie and H. F. King, *J. Chem. Phys.*, **47**, 564 (1967).