DEDICATION

To my parent Mr. and Mrs. G. R. Ungemach, with much love and appreciation.

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NOTICE
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CHEMICAL APPLICATIONS OF MOLECULAR QUANTUM THEORY

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ABSTRACT

Some fascinating aspects of several molecular systems of chemical interest are revealed with the aid of molecular quantum theory. The self-consistent field (SCF) method is used to predict the molecular structures of the very interesting ClF_2 , ClF_4 and Cl_3 radicals, and the ions ClF_2^+ , ClF_2^- , ClF_4^+ and ClF_4^- . The ClF_2 and Cl_3 radicals are predicted to be bent with bond angles of 145.2° and 158.6° , respectively, while the ions ClF_2^+ and ClF_2^- are predicted to be bent with a bond angle of 97.4° and linear, respectively. The geometry predictions for the ClF_4 radical and the ClF_4^+ ion are found to be notably basis set dependent. The ClF_4^- ion is predicted to be square-planar. Multi-configuration self-consistent field (MCSCF) calculations have yielded the dipole moment function for the $^1\Sigma^+$ state of HI , which qualitatively confirms the experimental finding that the dipole derivative at R_e is negative. The $^2\Sigma^+$ $\text{F} + \text{H}_2$ potential energy surface is studied extensively with the configuration interaction (CI) method. The most complete calculations yield an activation energy of 2.74 kcal/mole and an exothermicity of 30.0 kcal/mole. The production of a potential energy surface of "chemical accuracy" for this system is found to be more difficult than previously believed. The simplest hydrophobic model, the water-methane system, is studied with the SCF method in order to determine the nature and magnitude of the interaction. The most favorable geometric arrangement corresponds to an attraction of 0.5 kcal/mole.

I. GENERAL INTRODUCTION

It has become common practice for chemists to utilize theoretically derived information during the investigation of a wide variety of problems. In particular, a much greater understanding of chemical processes as they occur on the atomic and molecular levels has been achieved through the use of the quantum theory introduced in the early part of this century. It has since become clear that the existence of a sound theoretical description of atomic and molecular structure and interactions provides a useful means for the chemist to obtain knowledge of phenomena which might be difficult or impossible to study, otherwise. Furthermore, existing data of experimental origin may be compared with theoretical information and thus tested for validity; this is not only desirable, but essential if such experimental data are not readily produced.

It is, therefore, the purpose of the present work to investigate some chemically interesting molecular systems using a tool of the theoretical chemist; molecular quantum theory. Besides providing heretofore unavailable data concerning these molecular systems, this work provides an opportunity to subject both theoretical and experimental sources of information to critical evaluation, thereby making the process of scientific investigation more complete.

II. THEORETICAL BACKGROUND

1. Quantum Theory and the Closed Shell Self-Consistent Field Method

A great deal of physically significant information about molecular systems may be obtained from the solutions, $\psi_R(r)$, to the linear, second order, homogeneous differential equation

$$\left[h + V - E(R) \right] \psi_R(r) = 0 \quad (1)$$

where

$$h = \sum_{\mu=1}^{\# \text{ elec}} \left[-\frac{1}{2} \nabla_{\mu}^2 - \sum_{\alpha}^{\# \text{ nuc}} \frac{Z_{\alpha}}{r_{\alpha\mu}} \right] \quad (2)$$

$$V = \sum_{\alpha < \beta}^{\# \text{ nuc}} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}} + \sum_{\mu < \nu}^{\# \text{ elec}} \frac{1}{r_{\mu\nu}} \quad (3)$$

and $E(R)$ is the total molecular electronic energy in the clamped-nuclei (Born-Oppenheimer) approximation.¹ Eq. (1) is commonly known as the non-relativistic, time-independent, electronic Schroedinger equation. Obtaining solutions to Eq. (1) is of central importance² in theoretical chemistry. In order to better understand the significance of the solutions to Eq. (1), it is essential that one understands the nature of the equation itself.

In the present work, the molecules under consideration are regarded as conservative systems,³ i.e., ones in which the potential energy, V , is a function solely of coordinates and is related to all forces in the system by

$$\vec{F} = -\vec{\nabla} \cdot V \quad (4)$$

This is an important point, since classically, for a system with such a potential, the Hamiltonian function³ may be written as

$$H = \sum_{i=1}^{\# \text{ part}} q_i \frac{\partial T(\dot{q})}{\partial \dot{q}_i} - L(q, \dot{q}) \quad (5)$$

where, T, the total kinetic energy in generalized coordinates is

$$T(\dot{q}) = \frac{1}{2} \sum_{k,j} a_{kj} \dot{q}_k \dot{q}_j \quad (6)$$

and, L, the Lagrangian function is

$$L(q, \dot{q}) = T(\dot{q}) - V(q) \quad (7)$$

Since from Eq. (6) we see that $T(\dot{q})$ is a homogeneous function of order two, we may write

$$\begin{aligned} H(q, \dot{q}) &= \frac{1}{2} \sum_i q_i \left(\sum_j a_{ij} \dot{q}_j + \sum_k a_{ki} \dot{q}_k \right) - L(q, \dot{q}) \\ &= 2T - (T - V) \end{aligned} \quad (8)$$

$$= T + V$$

$$= E$$

Thus, for conservative classical systems, the Hamiltonian function is the total energy.

In quantum theory⁴, the Hamiltonian function corresponds to the Hamiltonian operator

$$H = T + V \longrightarrow H_{op} = T_{op} + V_{op} \quad (9)$$

or

$$H = \frac{1}{2m_i} \sum_i p_i^2 + V(q_i) \longrightarrow \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V_{op}(q_i) = H_{op} \quad (10)$$

where, in Cartesian coordinates,

$$\vec{p}_i = \hat{p}_{xi} + \hat{p}_{yi} + \hat{p}_{zi} \longrightarrow -\hbar \left[\hat{i} \frac{\delta}{\delta x_i} + \hat{j} \frac{\delta}{\delta y_i} + \hat{k} \frac{\delta}{\delta z_i} \right] = \vec{\nabla}_{op} \quad (11)$$

$$V(q_i) = V(x_i y_i z_i) \longrightarrow V_{op}(x_i y_i z_i) \quad (12)$$

Eq. (10) serves to define the Hamiltonian operator in three dimensions. The form of the potential energy operator, V_{op} , depends upon the system under consideration. Analogous to the Hamiltonian function of classical mechanics, the Hamiltonian operator of quantum mechanics is associated with the total energy of a system of particles. In order to determine the total energy, it is necessary to solve operator equations of the form

$$H_{op} u(q_i) = E u(q_i) \quad (13)$$

where $u(q_i)$ is some many-particle function of coordinates and E is the total energy. Eq. (13) is referred to as an eigenvalue equation. The solution to Eq. (13) is called an eigenfunction. The constant, E , is the eigenvalue of the operator, H_{op} . In the terminology of wave mechanics⁵, eigenfunctions specifying the behavior of N -particle systems are called wave functions, state functions or state vectors. The latter term stems from the fact that, in general, solutions to Eq. (13) reside in a complex, infinite-dimensional linear vector space called Hilbert space. In the notation of Dirac⁶, a state vector is symbolized as

$$|\psi\rangle = \text{ket vector}$$

and the corresponding dual vector is symbolized by

$$\langle\psi| = \text{bra vector}$$

Since $u(q_i)$ does not depend on time, it is referred to as a stationary state solution. All observable quantities of physical significance will be determined by solving eigenvalue equations similar to Eq. (13). Each physical observable is associated with a particular linear, quantum mechanical operator.⁷ Quantities which are constants of the motion satisfy the Heisenberg equation of motion for the particular operator concerned. Thus, for an arbitrary time-independent operator, A, the observable, a, will be a constant of the motion if

$$\frac{da}{dt} = \frac{1}{i\hbar} \langle\psi|[A,H]|\psi\rangle + \langle\psi|dA/dt|\psi\rangle = 0 \quad (14)$$

Hence, operators commuting with the Hamiltonian operator will have average (expectation) values which are time-independent. Finally, the full set of eigenvalues of an operator are said to constitute the spectrum of that operator.

In treating molecular systems it is practical to distinguish between nuclear and electronic "particles". For a molecular system, the Hamiltonian in atomic units⁸ is

$$-\frac{1}{2} \sum_{\alpha} \frac{\nabla_{\alpha}^2}{M_{\alpha}} - \frac{1}{2} \sum_{\mu} \nabla_{\mu}^2 - \sum_{\alpha, \mu} \frac{Z_{\alpha}}{r_{\alpha\mu}} + \sum_{\alpha < \beta} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}} + \sum_{\mu < \nu} \frac{1}{r_{\mu\nu}} \quad (15)$$

where the first term is the nuclear kinetic energy operator, the second term is the electronic kinetic energy operator, the third term is the nuclear-electronic potential energy operator; the fourth term is the internuclear potential energy operator; and the fifth term is the inter-electronic potential energy operator. The corresponding Schrodinger eigenvalue equation is

$$H_{op} \Psi(r, R) = E \Psi(r, R) \quad (16)$$

where $\Psi(r, R)$ is a function of both nuclear and electronic coordinates and spin. The total energy, E , relative to the molecular center of mass, is a sum of all internal, non-relativistic energies arising from electronic and nuclear motions and rotation of the nuclei. An inherent assumption

in Eq. (16) is that certain other interactions, e.g., those arising from electronic spin-orbit, nuclear-electronic spin-spin, etc., make a small enough contribution to the total energy that they may be neglected or treated as a perturbation, if desired.⁹

Ordinarily, the function, $\Psi(r,R)$ is written as

$$\Psi(r,R) = \psi_R(r)\phi(R) \quad (17)$$

where $\psi_R(r)$ is the electronic wave function describing the motion of the electrons in the field of the fixed nuclei. The nuclear wave function, $\phi(R)$, describes the vibrational and rotational motion of the nuclei in the potential field of the electrons. The approximation which allows us to write Eq. (17) is called the clamped-nuclei or Born-Oppenheimer approximation.¹

Using Eq. (17), we may write Eq. (16) as

$$\begin{aligned} H_{op}\psi_R(r)\phi(R) &= \left[T_R + h + V \right] \psi_R(r)\phi(R) \\ &= E\psi_R(r)\phi(R) \end{aligned} \quad (18)$$

where T_R represents the nuclear kinetic energy operator, while h and V are operators of the form shown in Eqs. (2) and (3). After eliminating T_R (zero nuclear kinetic energy) and dividing through by $\phi(R)$, Eq. (18) reduces to Eq. (1). In order to solve for the nuclear wavefunction, we substitute Eq. (1) into Eq. (18) to obtain

$$\left[T_R + E(R) \right] \psi_R(r) \phi(R) = W \psi_R(r) \phi(R) \quad (19)$$

where W is the approximate total energy. Dividing Eq. (19) by $\psi_R(r)$ yields

$$\left[T_R + E(R) \right] \phi(R) = W \phi(R) \quad (20)$$

Thus, we see that one may describe the nuclear motions using a suitable electronic potential which gives the electronic potential energy in the clamped-nuclei approximation.

The exact solutions to Eq. (1) are not obtainable due to the presence of the interelectronic potential energy terms, $1/r_{\mu\nu}$, in the Hamiltonian. The occurrence of these terms precludes the separation of the Schrodinger equation into ordinary differential equations in terms of any presently known coordinate system. However, one may produce approximate solutions to Eq. (1) using one of several theoretical methods.

The well-known variation theorem¹⁰ states that any trial function, which is an approximate solution to the Schroedinger equation will yield an energy which is an upper bound to the true energy of the system under consideration. Stated mathematically,

$$\begin{aligned} \langle H \rangle &= \frac{\langle \psi_{\text{approx}} | H | \psi_{\text{approx}} \rangle}{\langle \psi_{\text{approx}} | \psi_{\text{approx}} \rangle} \\ &= W \geq E_{\text{exact}} \end{aligned} \tag{21}$$

where the quantity $\langle H \rangle$ is the expectation value of the Hamiltonian operator, and is the value of the energy obtained using an arbitrary wavefunction which is not necessarily an eigenfunction of the Hamiltonian.

It is important to note that, according to Eq. (21) the best wavefunction will be that which yields the lowest value of $\langle H \rangle$. However, this wavefunction is not necessarily the optimum in terms of other observables of the system (i.e., physical properties).

The most widely used and best studied variational method is the Hartree-Fock-Roothaan self-consistent field method.¹¹ In this method the trial function, ψ_{approx} , referred to as a Slater determinant¹² is an anti-symmetrized product of one-particle molecular spin orbitals (MSO's)

$$\psi_{\text{approx}} = \frac{1}{(N!)^{\frac{1}{2}}} \begin{vmatrix} \phi_1(1)\phi_2(1)\dots\phi_N(1) \\ \phi_1(2)\phi_2(2)\dots\phi_N(2) \\ \vdots \\ \phi_1(N)\phi_2(N)\dots\phi_N(N) \end{vmatrix} \quad (22)$$

where each MSO is given by the product of a spatial function (molecular orbital or MO) and a spin function

$$\psi_i = \phi_i(\vec{r}) w(s) \quad w(s) \in \{\alpha, \beta\} \quad (23)$$

The functions $\phi_i(\vec{r})$, are usually chosen to be orthonormal

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \quad (24)$$

where the brackets indicate that integration is to be carried out over all coordinate space. The task then amounts to finding the best $\{\phi_i\}$ to use in the total wavefunction of Eq. (22).

In a closed-shell system consisting of $2N$ particles occupying N MO's, the electronic energy associated with a wavefunction of the form shown in Eq. (22) is

$$E = 2 \sum_{i=1}^N h_{ii} + \sum_{i,j}^N (2J_{ij} - K_{ij}) \quad (25)$$

where

$$h_{ii} = \langle \phi_i | -\frac{1}{2}\nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha i}} | \phi_i \rangle \quad (26)$$

$$J_{ij} = \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_i(1)\phi_j(2) \rangle \quad (27)$$

$$K_{ij} = \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_i(2)\phi_j(1) \rangle \quad (28)$$

The h_{ii} are one-electron integrals, and the J_{ij} and K_{ij} are two-electron coulomb and exchange integrals, respectively.

By requiring that the first order variation in E be zero, with the constraint that the $\{\phi_i\}$ remain orthogonal, we may obtain the Hartree-Fock-Roothaan equations

$$F_{op}|\phi_i\rangle = \lambda_{ii}|\phi_i\rangle + \sum_{j \neq i} |\phi_j\rangle \lambda_{ji} \quad (29)$$

or in matrix notation

$$F_{\sim} \phi_{\sim} = \phi_{\sim} \lambda_{\sim} \quad (30)$$

where the Fock operator, F_{op} , is defined by

$$F_{op} = h_{op} + G_{op} \quad (31)$$

$$h_{op} = -\frac{1}{2} \nabla_{\mu}^2 - \sum_{\alpha}^{\# \text{ nuc}} \frac{Z_{\alpha}}{r_{\alpha\mu}} \quad (32)$$

$$G_{op} = \sum_{j=1}^N 2J_j - K_j \quad (33)$$

We may define the coulomb and exchange operators

$$J_i |\phi_j(2)\rangle = \langle \phi_i(1) | 1/r_{12} | \phi_i(1) \rangle |\phi_j(2)\rangle \quad (34)$$

$$K_i |\phi_j(2)\rangle = \langle \phi_i(1) | 1/r_{12} | \phi_j(1) \rangle |\phi_i(2)\rangle \quad (35)$$

The matrix, λ , is the matrix of Lagrange multipliers included in the energy functional to insure the orthogonality of the MO's. The multiplier matrix may be shown to be Hermitian (i.e., $\lambda_{ij} = \lambda_{ji}^*$).

By choosing an appropriate unitary transformation, we may render the Lagrangian multiplier matrix diagonal thereby reducing Eq. (30) to

$$F_{\sim} \phi' = \epsilon'_{\sim} \phi' \quad (36)$$

The diagonal elements of ϵ , commonly called orbital energies, are then the eigenvalues of F_{op} in the chosen elementary basis. For a given set of doubly occupied MO's, the orbital energy, ϵ_{ii} , corresponds to the approximate ionization potential of the i^{th} MO.

Eqs. (36) are referred to as pseudo-eigenvalue equations since F_{op} is constructed from the MO set $\{\phi_i\}$. We must take care, however, to note that the unitary transformation which diagonalizes λ also leaves the operator F_{op} and the wavefunction invariant.

The Hartree-Fock-Roothaan method is very conveniently formulated in matrix notation^{11,13}. As before, the MO's are represented as a row matrix

$$\phi_{\sim} = (\phi_1 \phi_2 \dots \phi_N) \quad (37)$$

Furthermore, in practice, one usually analytically expands each MO in a finite, linear combination of elementary functions (basis functions or atomic orbitals, AO's) centered on each of the atoms composing the molecular system of interest as follows

$$\phi_i(r) = \sum_{\mu=1} \chi_{\mu} c_{\mu i} \quad (38)$$

or in matrix notation

$$\phi_i(r) = \underset{\sim}{\chi} \underset{\sim}{C}_i \quad (39)$$

where $\underset{\sim}{\chi}$ is a row matrix and $\underset{\sim}{C}_i$ is a column matrix. It is no exaggeration to say that the choice of $\{\chi_{\mu}\}$ is perhaps the single most important aspect of any quantum mechanical calculation. Clearly, the nature of the system being investigated is directly reflected by the choice of the elementary functions used to describe the system.

A good elementary basis function for linear molecules is the Slater-type function (STF)¹⁴. It has the form

$$\chi = N(r) n^{r-1} e^{-\zeta r} Y_{lm}(\theta, \phi) \quad (40)$$

where ζ is the orbital exponent. Another commonly used basis function is the Gaussian-type function (GTF). It is inferior to the STF because it has the wrong behavior near the nucleus. However, a sufficiently large number of GTF's can approximate an STF quite satisfactorily. In Cartesian coordinates a GTF has the form

$$\chi_{\mu} = C_{\mu} x^n y^m z^l e^{-\alpha r^2} \quad (41)$$

where n, m , and l are integers chosen to produce the desired angular properties of χ . The orbital exponent is α .

In the analytical (also called the linear combination of atomic orbitals (LCAO)) SCF method, the task is to find the best set of vectors, $\{C_i\}$, with which to represent each MO in the total wavefunction.

In the LCAO-MO-SCF formalism presented by Roothaan¹¹, equations (25), (29) and (30) become

$$E = 2 \sum_i C_i^\dagger h C_i + \sum_{ij} C_i^\dagger (2J_{ij} - K_{ij}) C_i \quad (42)$$

$$F C_i = S \sum_j C_j \lambda_{ji} \quad (43)$$

$$F C = S C \lambda \quad (44)$$

where the column vectors, C_i , are defined in equations (38) and (39).

An element of the overlap matrix, S , is given by

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$

An element of the Fock matrix is given by

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} D_{\lambda\sigma} (J_{\mu\nu} - \frac{1}{2}K_{\mu\nu}) \quad (45)$$

where

$$h_{\mu\nu} = \langle \chi_\mu | h | \chi_\nu \rangle \quad (46)$$

$$J_{\mu\nu} = \langle \chi_\mu(1)\chi_\lambda(2) | 1/r_{12} | \chi_\nu(1)\chi_\sigma(2) \rangle \quad (47)$$

$$K_{\mu\nu} = \langle \chi_\mu(1)\chi_\nu(2) | 1/r_{12} | \chi_\lambda(1)\chi_\sigma(2) \rangle \quad (48)$$

and

$$D_{\lambda\sigma} = 2 \sum_{i=1}^{\# \text{ occ. orb.}} c_{\lambda i} c_{\sigma i} \quad (49)$$

The matrix, D , is the representation of the first order reduced density function.

We may place Eq. (44) in a more practical form by the application of a transformation, T , obtained by diagonalizing the overlap matrix, S , with U as follows

$$T^T F T (\tilde{T})^{-1} C = T^T S T (\tilde{T})^{-1} C \lambda \quad (50)$$

or

$$F' C' = C' \lambda \quad (51)$$

where

$$\underset{\sim}{F}' = \underset{\sim}{T} \underset{\sim}{F} \underset{\sim}{T} \quad (52)$$

$$\underset{\sim}{C}' = (\underset{\sim}{T})^{-1} \underset{\sim}{C} \quad (53)$$

$$\underset{\sim}{T} = \underset{\sim}{S}^{-\frac{1}{2}} \underset{\sim}{U} \quad (54)$$

$$(\underset{\sim}{T})^{-1} = \underset{\sim}{S}^{\frac{1}{2}} \underset{\sim}{U} \quad (55)$$

By choosing $\underset{\sim}{C}'$ so that the matrix, $\underset{\sim}{\lambda}$, is diagonal, we obtain a set of eigenvectors which satisfy the equations

$$\underset{\sim}{F}'_{op} \underset{\sim}{C}'_i = \epsilon_{ii} \underset{\sim}{C}'_i \quad i = 1, 2, \dots, N \quad (56)$$

where ϵ_{ii} is the energy of the i^{th} MO. The $\underset{\sim}{C}'_i$ are transformed by

$$\underset{\sim}{C} = \underset{\sim}{T} \underset{\sim}{C}' \quad (57)$$

and the $\tilde{C}_i$ are used to construct a new F_{op} by the prescription of Eq. (45). After the first SCF iteration, F_{op} may be transformed by the matrix of eigenvectors, $\tilde{C}$. Thus, for the second and remaining iterations,

$$\tilde{F}'_{op} = \tilde{C}^k \tilde{F}_{op} \tilde{C}^k \quad (58)$$

$$\tilde{C}^{k+1} = \tilde{C}^k \tilde{C}'^{k+1} \quad (59)$$

The construction, transformation and diagonalization process usually continues until the total SCF energy changes by less than some predetermined amount (commonly $0(10^{-7})$). At this point, the final set of eigenvectors, $\tilde{C}$, corresponding to N occupied MO's is produced as shown in Eq. (57).

2. Configuration Interaction and Electron Correlation

Although the SCF wavefunction is satisfactory for many purposes, it has one major flaw; by restricting the total number of electrons to a single, variationally determined set of one-particle spin-orbitals, the quality of electron correlation is omitted. A better variational wavefunction should allow for the instantaneous interactions between electrons (i.e., electron correlation)¹⁵.

From a set of M one-particle orbitals, there are

$$N = \prod_{i=1}^{p+q=M} \frac{(2\lambda_i)!}{n_i! (2\lambda_i - n_i)!} \quad (60)$$

possible Slater determinants which may be constructed from a given orbital occupation where, p is the number of occupied orbitals, n_i is the occupation number of the i^{th} orbital, and λ_i is the degeneracy of the i^{th} orbital. A general method which variationally determines a wavefunction constructed from a linear combination of Slater determinants is the configuration interaction (CI) method.^{2,16}

The CI wavefunction is expressed as

$$\Psi = \sum_I C_I \Phi_I \quad (61)$$

where Φ_I is a linear combination of Slater determinants formed so as to be eigenfunctions of the spin and symmetry operators of the electronic state under consideration. Each of the Φ_I is called a configuration state function (CSF)¹⁷. The coefficients, C_I , in Eq. (61) are determined variationally by solving the secular equation

$$\det(\tilde{H} - E) \tilde{C} = 0 \quad (62)$$

where, in matrix notation, an element of H is

$$H_{IJ} = \langle \phi_I | H | \phi_J \rangle \quad (63)$$

If, Ψ in Eq. (61), is constructed from all possible configurations, ϕ_I , formable from the chosen one-particle basis, then it is called a complete CI wavefunction. A complete CI wavefunction is an exact solution to the electronic Schroedinger equation in the space of configurations constructed from the chosen set of one-particle functions. Presently, however, it is impractical¹⁷ to calculate complete CI wavefunctions for systems with more than 3 or 4 electrons. Furthermore, most chemical processes may be studied with a high degree of accuracy using a truncated CI wavefunction obtained by carefully choosing a set of configurations which approximates the complete CI wavefunction. The set of configurations which spans a truncated space is usually generated² by exciting one or more electrons from a set of zeroth order (reference) configurations into a virtual one-particle space. From the generated set of CSF's, those which are retained (to first order) have a non-zero matrix element with the zeroth order subspace. Thus, in the Rayleigh-Schroedinger sense

$$\Psi_{\text{approx}} = \Psi^{(0)} + \Psi^{(1)} \quad (63)$$

$$= \Psi^{(0)} + \sum_J \phi_J \quad (64)$$

where

$$\langle \phi_j | H | \psi^{(0)} \rangle \neq 0 \quad (65)$$

Two important aspects of a CI calculation are the choice of the zeroth order subspace and the one-particle basis. The zeroth order subspace is ordinarily composed of configurations which are needed to adequately describe the chemical process being studied plus those which are deemed essential on the basis of experience. The latter criterion for choosing CSF's to be used in $\psi^{(0)}$ often requires a certain amount of experimentation depending upon the complexity of problem involved.

To illustrate a typical procedure for selecting the set of zeroth order CSF's and the starting orbitals for the one-particle space, consider a calculation of the $X^1\Sigma^+$ state of HF performed in the present work. The following CSF's are needed to describe the dissociation of HF to the correct, neutral atomic states, $H(^2S_g)$ and $F(^2P_u)$

$$\phi_1 = 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 \quad (66)$$

$$\phi_2 = 1\sigma^2 2\sigma^2 4\sigma^2 1\pi^4 \quad (67)$$

where the first CSF is the Hartree-Fock configuration and is the dominant CSF in the total CI wavefunction. The set of configurations composed of CSF's (66) and (67) form the zeroth order subspace (reference subspace). The zeroth order subspace is not to be confused with a zeroth order wavefunction. Using CSF's (66) and (67), a zeroth order wavefunction would be constructed as follows

$$\psi^{(0)} = C_1 \phi_1 + C_2 \phi_2 \quad (68)$$

The mixing coefficients, C_1 and C_2 , would be determined so as to satisfy the equation

$$H_{op}^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad (69)$$

The one-particle basis used for the generation of the n-particle space was produced by performing multi-configuration SCF (MCSCF)¹⁸ calculations (which included only CSF's (66) and (67)) of the $X^1\Sigma^+$ state of HF. The MCSCF calculations variationally determined the elementary function expansion coefficients of the MO's and produced a set of unoccupied (virtual) MO's. The complete set of one-particle functions, both occupied and virtual, was used to construct the n-particle space from the zeroth order subspace. A number of methods exist for producing

an n-particle space from a zeroth order subspace. Using the method of McLean and Liu¹⁹, a total of 4139 CSF's were produced with an elementary basis of six-s, four-p, three-d and one-f Slater-type functions centered on fluorine and three-s, two-p and one-d Slater-type functions centered on hydrogen. The total one-particle basis of MO's was, therefore, 20σ , 11π , 5δ and 1ϕ orbitals in linear molecule notation. The results of CI calculations of the $\chi^1\Sigma^+$ state of HF are shown in Table I, together with experimental data.

It is worth noting that if all possible excitations of a certain type (e.g., all single or double, or single and double excitations, etc.) are made from the zeroth order subspace into the entire virtual subspace of the one-particle space, then the choice of virtual orbitals is entirely arbitrary (as long as they span an orthogonal space). In other words, if desired, the virtual orbital expansion coefficients could be generated by orthonormalizing a set of one-particle functions which had unit expansion coefficients. In such a case, it follows that since the total wavefunction is a variationally determined construct, it is also invariant under a unitary transformation of the virtual subspace.

After carrying out a CI calculation, it is possible to produce a new set of one-particle functions which may be used to compact the list of CSF's. The new functions are called natural orbitals (NO's)^{9,20}. They are related to the initial set of molecular orbitals by a unitary transformation

$$\begin{matrix} V \\ \sim \end{matrix} = \begin{matrix} \phi \\ \sim \end{matrix} \begin{matrix} U \\ \sim \end{matrix} \quad (70)$$

where the matrix of NO's is $\tilde{V}$. The unitary transformation matrix, $\tilde{U}$, is that which renders diagonal the first order reduced density matrix, $\tilde{\gamma}$. Thus,

$$\tilde{U}^\dagger \tilde{\gamma} \tilde{U} = \tilde{n} \quad (71)$$

where $\tilde{n}$ is a diagonal matrix of occupation numbers. The elements of $\tilde{n}$ satisfy the following conditions

$$0 \leq n_i \leq 2\lambda_i \quad (72)$$

$$N = \sum_i n_i = \text{total \# electrons} \quad (73)$$

$$\lambda_i = \text{degeneracy of the } i^{\text{th}} \text{ NO} \quad (74)$$

In Table II are shown the NO occupation numbers from the first natural orbital transformation performed on the one-particle basis used in the 4139 CSF CI calculation of the $\chi^1\Sigma^+$ state of HF. The natural orbitals indirectly contain important information present in the initial CI wavefunction. In this respect, natural orbitals are an improved one-particle

basis. By forming the n-particle space from natural orbitals having occupation numbers greater than zero or some small value, one may effect a reduction in the size of the n-particle space. The repeated calculation of a CI wavefunction with the use of natural orbitals obtained from an immediately preceeding calculation is referred to as the iterative natural orbital CI (INO-CI) method²¹ and has been used considerably in past work.

If a more severe truncation of the n-particle space is desired, it is possible to delete CSF's on the basis of an energy criterion. Thus, a possible procedure would be to first select a set of NO's with occupation numbers greater than a specific value and construct an n-particle space. One would then perform a series of CI calculations by deleting orbitals (and, hence, CSF's) from this chosen set and noting at which point the total energy changes become significantly large. A technique similar to this is used in the present work on the ${}^2\Sigma^+ \text{ F} + \text{H}_2$ potential energy surface to truncate a CI wavefunction with respect to higher than double excitations.

Another useful technique employed in the present work to calculate a CI wavefunction relies upon a perturbative scheme. The method of generating the zeroth order subspace and choosing a set of one-particle functions is identical to that described previously. However, instead of immediately solving the secular equation (62), one first solves for the Rayleigh-Schroedinger first order perturbed wavefunction

$$\psi_{\text{total}} = \psi_I^{(0)} + \sum_{J \neq I}^N \frac{H_{JI}}{E_I^{(0)} - E_J^{(0)}} \phi_J \quad (75)$$

where $\Psi_I^{(0)}$ is the zeroth order wavefunction satisfying Eq. (69) and H_{JI} is the matrix element of H_{op} between the zeroth order wavefunction and the J^{th} configuration. The elements of H needed to determine the first order perturbed wavefunction are illustrated in Fig. 1. The next step is to construct and diagonalize the first order reduced density matrix and transform the initial orbital basis to produce a set of NO's. Based upon an examination of the NO occupation numbers, one may then effect a truncation of the initial CI wavefunction and proceed to solve the secular equation using the selected NO's as the set of one-particle orbitals. Incidentally, one may decide to form only the virtual subspace from the NO's if the occupied orbitals used initially are of high enough quality (as they may be if obtained from a good MCSCF calculation).

It is readily seen that the perturbative approach to calculating CI wavefunctions is of great value if one has a large n-particle space which makes a straight CI calculation impractical. The perturbative scheme allows one to calculate a smaller CI wavefunction which retains much of the quality present in a larger CI wavefunction.

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TABLE I

COMPARISON OF RESULTS FROM CALCULATIONS OF THE $X^1\Sigma^+$ STATE OF HF.

	2 CSF MCSCF	4139 CSF CI	1934 CSF CI ¹	Experiment ³
Electronic Energy	-100.0935	-100.3468 ²	-100.2645 ²	---
R_e , Å	0.9177	0.9187	0.9181	0.9170
D_e , eV	4.96	5.91	6.05	6.12

¹ CSF's generated by exciting one or two electrons from the 2σ orbital into the external space were deleted from this wavefunction.

² 1σ orbital doubly occupied in all CSF's.

³ ref [22]

TABLE II

NATURAL ORBITAL OCCUPATION NUMBERS FROM THE 4139 CSF CI CALCULATION OF THE $X^1\Sigma^+$ STATE OF HF. THE 1σ ORBITAL WAS DOUBLY OCCUPIED IN ALL CSF'S.

ORBITAL SYMMETRY				
Orbital	σ	π	δ	ϕ
1	2.00000	3.95105	0.00918	0.00076
2	1.98713	0.02832	.00090	
3	1.96566	.00962	.00076	
4	0.02617	.00160	.00012	
5	.00843	.00124	.00009	
6	.00483	.00075		
7	.00114	.00021		
8	.00079	.00012		
9	.00039	.00007		
10	.00033	.00002		
11	.00012	.00002		
12	.00010			
13	.00004			
14	.00002			
15	.00002			
16	.00001			
17	.00001			
18	.00000			
19	.00000			
20	.00000			

FIGURE CAPTION

Fig. 1 CI matrix elements needed for perturbation calculation.

XBL 7710-6813

III. MOLECULAR STRUCTURE OF THE ClF_2 , ClF_4 , and Cl_3 RADICALS

1. Introduction

The ClF_2 and ClF_4 radicals are two interesting interhalogen molecules with 21 and 35 valence electrons, respectively. Until recently, most research has focused on the stable, relatively well-known^{1,2} chlorine fluorides ClF , ClF_3 and ClF_5 . The ClF molecule in the $X^1\Sigma^+$ electronic state has a spectroscopic dissociation energy of 60.4 kcal/mole, a bond length of 1.63Å and a dipole moment of 0.888D (Cl^+F^-).^{3,4} The planar trigonal ClF_3 molecule in the 1A_1 electronic state has the structure⁵

and a dipole moment of 0.557D.⁶ The ClF_5 molecule is less well characterized than ClF or ClF_3 , but it is thought to have the shape of a square pyramid⁷ with axial and basal bond lengths of 1.62Å and 1.72Å, respectively.

By comparison, little is known of the chlorine fluorides with an odd number of electrons. Mamantov et al.⁸ originally prepared ClF_2 by photolyzing mixtures of ClF and F_2 and freezing the products in an inert gas matrix of Ar or N_2 . Based upon the observed IR spectrum of the photolyzed mixtures, Mamantov et al. assigned the frequencies⁹ $\nu_1 = 536\text{cm}^{-1}$

(symmetric stretch), $\nu_2 = 575\text{cm}^{-1}$ (asymmetric stretch) and $\nu_3 = 242\text{cm}^{-1}$ (bending) to vibrational modes of a bent, symmetrical ClF_2 molecule. Using the assigned frequencies, they determined a bond angle of $136^\circ \pm 15^\circ$ or $144^\circ \pm 15^\circ$, with the latter value being arrived at through the use of computer simulated frequencies. Blauer et al.¹⁰, assuming a bent structure for ClF_2 , have examined the thermal decomposition of ClF_3 and determined a value of $\Delta H_0^\circ(\text{ClF}_2)$ of -19 ± 2 kcal/mole. Krogh and Pimentel¹¹ have suggested that ClF_2 occurs as an intermediate species in the $\text{ClF}_3\text{-H}_2$ and $\text{ClF}_3\text{-CH}_4$ chemical laser systems. Their view of ClF_2 as a linear molecule is compatible with Nelson and Pimentel's¹² conclusion that the related Cl_3 radical has a linear, slightly asymmetric structure. Using crossed molecular beams of D and ClF_3 , Cross¹³ has determined that ClF_2 may be produced by the reaction

for mean collision energies of ~ 10 kcal/mole. Only a single semi-empirical CNDO/2 calculation¹⁴ has been reported for the ClF_2 and Cl_3 radicals. The results are essentially inconclusive and suggest the need for more accurate ab initio calculations.

Morton and Preston¹⁵ have recently recorded the ESR spectrum of ClF_4 produced by the photolysis of a solution of Cl_2 or HCl and CF_3OF or SF_3OF . Based on the ESR spectrum of such a photolyzed solution, Morton

and Preston concluded that ClF_4 belongs to D_{4h} point group and has a ${}^2A_{1g}$ ground electronic state. Gregory¹⁶ has performed semi-empirical CNDO and INDO calculations on ClF_4 and predicts it to be planar (${}^2A_{1g}$ electronic state) or slightly non-planar with a small ($1\text{-}4\text{cm}^{-1}$) barrier to inversion.

There have been a number of experimental studies¹⁷⁻²⁸ of the singly-charged ions of ClF_2 and ClF_4 . Christie and co-workers¹⁸ have recorded the vibrational spectra of $\text{ClF}_2^+\text{AsF}_6^-$ (IR and Raman) and $\text{ClF}_2^+\text{BF}_4^-$ (IR). Based on these spectra, the bond angle of ClF_2^+ was limited to the range $90^\circ\text{-}120^\circ$. Christie *et al.*¹⁹ have also recorded the vibrational spectra of $\text{NO}^+\text{ClF}_2^-$ (IR), $\text{Cs}^+\text{ClF}_2^-$ (IR) and $\text{Rb}^+\text{ClF}_2^-$ (IR and Raman) and concluded that a linear, centro-symmetric structure for ClF_2^- is consistent with the observation of only a single Raman band in the spectrum of $\text{Rb}^+\text{ClF}_2^-$. They also note¹⁹ that ClF_2^- experiences distortion and/or lowering of site symmetry in $\text{Cs}^+\text{ClF}_2^-$ and $\text{Rb}^+\text{ClF}_2^-$ due to crystal field effects.

Both vibrational²⁴ and ${}^{19}\text{F}$ NMR²³ spectra of ClF_4^+ have been measured. Both spectra are consistent with a C_{2v} structure for ClF_4^+ similar to that of the isoelectronic SF_4 molecule.²⁸ The same research group²⁵⁻²⁷ has studied the ClF_4^- molecule and concluded that Raman, infrared and conductivity measurements show ClF_4^- to be square-planar in the $\text{Rb}^+\text{ClF}_4^-$ and $\text{Cs}^+\text{ClF}_4^-$ complexes. Infrared measurement²⁵ indicates a lower symmetry for ClF_4^- in $\text{NO}^+\text{ClF}_4^-$.

Previous *ab initio* calculations on the ions ClF_2^+ , ClF_2^- , ClF_4^+ and ClF_4^- have been reported by Guest, Hall and Hillier.²⁹ They performed calculations using a minimum basis set of Gaussian functions augmented by a set of d functions on chlorine. By fixing the Cl-F bond

lengths at 1.66Å, Guest et al. predicted the bond angles of the above four ions.

In addition to the above molecules, the Cl_3 radical is also examined in the present work. The trichloride radical, which like the ClF_2 radical, possesses 21 valence electrons, has been reported in a matrix isolation study.¹² Based on the observed vibrational spectrum of a photolyzed mixture of Kr and Cl_2 , it was concluded that Cl_3 radical is linear. This conclusion conflicts indirectly with the findings of Mamantov and co-workers⁹ that the electronically similar ClF_2 radical is bent.

Thus, it is the object of the present theoretical research to make a priori predictions of the structures of ClF_2^+ , ClF_2 , ClF_2^- , ClF_4^+ , ClF_4^- , ClF_4 and Cl_3 . Although structures for all seven of these species have been proposed, none has been precisely determined.

2. Computational Details

All computations reported in this part of the thesis were carried out within the self-consistent field (SCF) approximation. Four different basis sets were used. Shown in Table I is the initially used minimum basis set (MBS). The MBS consisted of 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, and $3p_z$ Slater-type orbitals (STO) on Cl and 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ STO on F. Each STO was represented by a least squares fit³⁰ to four Gaussian-type functions (GTF). The MBS is usually adequate for predicting geometries, although there are some exceptions.^{31,32} Calculations with the MBS were performed on all of the molecules in the present study. In Table II is shown the second basis set used. This set, termed a double zeta (DZ) basis set, contains twice as many STO as the MBS. Each STO

in the DZ basis was represented by Gaussian functions contracted according to Dunning for the chlorine³³ and fluorine³⁴ atoms. Hence, we may denote the Cl and F DZ basis sets by (12s9p/6s4p) and (9s5p/4s2p), respectively, where the first pair of numbers in brackets represents GTF and the second pair of numbers indicates the contracted STO. The DZ basis is generally quite accurate³² for predicting geometries. This basis set was also used in calculations on all of the molecules in the present work.

Table III shows the third, extended (EXT) basis set. In this set, the chlorine and fluorine p orbitals were contracted in a more flexible fashion to allow for their distortion in the molecular framework. The Cl and F extended basis sets may be denoted (12s 9p/6s 5p) and (9s 5p/4s 3p), respectively. Thus, for chlorine, nine p-GTF were contracted 5 3 1 1 to represent five p-STO, and, for fluorine, five p-GTF were contracted 3 1 1 to represent three p-STO. The EXT basis was used only in calculations performed on the ClF₂ radical.

The fourth basis was the double zeta plus polarization (DZ + P) basis set. This set is simply the double zeta basis supplemented by the six d-GTF, x^2 , y^2 , z^2 , xz , yz and xy (orbital exponents 0.6) on chlorine. The DZ + P basis was used in calculations performed on ClF₂, ClF₄, ClF₄⁺ and Cl₃.

The calculations carried out in this work were on the restricted Hartree-Fock type.³⁵ Computations were completed using the Cal Tech-Ohio State-Berkeley version of the SCF program POLYATOM.³⁶ Some initial calculations were also completed with the program Gaussian 70.³⁷

3. Molecular and Electronic Structure Predictions

A. Triatomic Molecules

Geometry predictions for the ions and radicals are given in Tables IV and V, respectively. Orbital energies are listed in Table VIII.

Calculations performed on ClF_2^+ indicate a $^1\text{A}_1$ ground electronic state corresponding to a bent molecule with a bond angle of 98.2° (minimum basis) or 97.4° (double zeta basis). These values are within the range of 90° - 120° predicted by Christie and co-workers¹⁸ from vibrational data. Furthermore, there is excellent agreement between the present results and the value of 98.2° determined by Guest *et al.* for the F-Cl-F bond angle. The Cl-F bond length determined with the minimum and double zeta basis sets was 1.72Å and 1.70Å, respectively. It should be noted, however, that the double zeta basis is known to predict an internuclear separation in the ClF molecule ($X^1\Sigma^+$ electronic state) of 1.72Å. This differs from the experimental value⁴ of $R_e(\text{ClF})$ by +0.09Å. The inclusion of d functions ($\alpha = 0.6$) on chlorine results in the prediction of an internuclear separation for ClF of 1.64Å, which is in excellent agreement with the experimental value. Thus, it is expected that one must include d functions on chlorine in order to predict accurate bond lengths for ClF_2^+ .

Qualitatively,³⁸⁻⁴² one would predict ClF_2^+ to be bent, having a bond angle of $\sim 100^\circ$ and a structure such as

where the two lone pairs of electrons, which occupy the $3\pi_u$ orbital in linear ClF_2^+ , occupy the greatly delocalized $8a_1$ and $3b_1$ orbitals in C_{2v} ClF_2^+ . From MO and group theoretical considerations, one would expect ClF_2^+ to have a total of eight a_1 , one a_2 , three b_1 , and five b_2 orbitals fully occupied in the 1A_1 single-determinant Hartree-Fock wavefunction. One would also expect ClF_2^+ to be electronically and structurally similar to the isoelectronic SF_2 molecule⁴³. The SF_2 molecule is known⁴³ to have a bond angle of 98.3° and a bond length of $1.59\text{\AA}$. Thus, it is seen that the SF_2 bond angle differs by only $+0.9^\circ$ from that calculated for ClF_2^+ with the double zeta basis. Further, it is reasonable to assume that the addition of chlorine d functions ($\alpha=0.6$) to the DZ basis would result in the calculation of a Cl-F bond length of $1.59\text{\AA} - 1.60\text{\AA}$, which is comparable to the bond distance of $1.59\text{\AA}$ determined experimentally for SF_2 .

The ClF_2^- ion is predicted to have a $^1\Sigma_g^+$ ground electronic state corresponding to a linear, centro-symmetric structure. The theoretical determination of a linear geometry for ClF_2^- is consistent with the experimental observations of Christie and co-workers¹⁹ and the theoretical prediction of Guest, Hall and Hillier.²⁹ The calculated Cl-F bond lengths of $1.87\text{\AA}$ (minimum basis) and $1.93\text{\AA}$ (double zeta basis) are quite long compared with the bond distances in the molecules ClF , ClF_3 , and ClF_5 . One would, however, qualitatively predict³⁹⁻⁴² a lengthening (relative to neutral ClF_2) of the Cl-F bond to accompany the formation of the negative ion of ClF_2 . The effect of increased repulsion between non-bonding and bonding electron pairs (valence-shell electron pair repulsion

or VSEPR model) in ClF_2^- would be to shift the bonding electrons farther away (out) from the central atom, thus increasing the bond length.

Since ClF_2^- is an AB_2 molecule possessing 22 valence electrons, arguments based upon Walsh's rules³⁸ would predict a linear geometry for this ion. In addition, one could picture ClF_2^- in a qualitative fashion as having the structure

where three lone pairs of electrons are situated symmetrically in a plane perpendicular to the molecular axis. Of course, in the linear molecule notation of the $D_{\infty h}$ point group, the lone pairs occupy the $3\pi_u$ and $6\sigma_g$ molecular orbitals. It is reasonable to expect the electron occupancy of ClF_2^- to be similar to that of the hypothetical ArF_2 molecule, which, based upon elementary MO and group theoretical principles, would most likely have the electron occupancy

The ClF_2 radical is predicted to be linear ($^2\Sigma_g^+$ electronic state) with the minimum basis set and bent (2A_1 electronic state) with a bond angle of 145.2° (DZ and EXT basis sets) or 148.8° (DZ + P basis set). The calculated energy difference between the optimized linear and bent forms of ClF_2 is 7.7 kcal/mole with the DZ and EXT basis sets and 9.8 kcal/mole with the DZ + P basis set. Thus, it is seen that all of the larger basis sets consistently predict ClF_2 to be significantly bent with a bond angle consistent with the value of $140^\circ \pm 19^\circ$ determined experimentally by Mamantov and co-workers.⁹ The clear conflict between the minimum basis set prediction and those of the larger bases is somewhat distressing in the absence of any accurate experimental determination of the structure of an AB_2 molecule with 21 valence electrons. One would, of course, tend to favor the geometry predictions of the larger, more complete basis sets. Conceivably, the minimum basis set simply lacks the flexibility needed to accurately describe the molecular structure of the ClF_2 radical. However, in order to examine this possibility, it is necessary to compare additional data obtained with the MBS and the larger basis sets. With this in mind, calculations of the lowest lying excited state of ClF_2 were carried out with the minimum and double zeta basis sets. This state, predicted to be linear and of $^2\Pi_u$ symmetry with both basis sets, has the electron occupancy

The Cl-F bond length in ${}^2\Pi_u$ ClF_2 was determined to be 1.79Å (MBS) or 1.83Å (DZ). These values are comparable to the Cl-F distances calculated for the 2A_1 state of ClF_2 . One prediction for which the minimum and double basis sets differ markedly is the excitation energy $\Delta E({}^2A_1 \longrightarrow {}^2\Pi_u)$. The minimum basis set yields a value of 3.08 eV for ΔE , whereas $\Delta E = 0.91$ eV with the DZ basis. The latter value would, of course, be the more trustworthy in the absence of any experimental results. Another distinct difference between the minimum and DZ basis sets concerns the ClF_2^- ion. Here, the MBS indicates that ClF_2 is more stable electronically by 3.62 eV than ClF_2^- , and the DZ basis shows ClF_2 to be less stable than ClF_2^- by 5.08 eV. Hence, there is further indication that the minimum basis differs in a serious qualitative respect from the larger bases.

In attempting to understand the shape of the ClF_2 radical as predicted by the larger basis sets, there are at least three factors which bear consideration. It is the subtle interplay of these factors which determines the structure of ClF_2 .

a) During the symmetrical bending of linear ClF_2 an increase in electronic stability is achieved by the delocalization of the $3\pi_u$ lone pairs (LP) of electrons. These LP's are primarily localized in the space of the chlorine $3p_x$ and $3p_y$ atomic orbitals in linear ClF_2 . In C_{2v} ClF_2 the $3\pi_u$ MO becomes the $8a_1$ and $3b_1$ orbitals. Associated with the delocalization is a decrease in the energies of the latter orbitals.

b) In linear ClF_2 the $6\sigma_g$ MO is a singly occupied non-bonding orbital. As ClF_2 assumes a C_{2v} structure, the $6\sigma_g$ MO becomes the $9a_1$ orbital. The latter orbital possesses a significant amount (31% - DZ

calculation) of chlorine $3p_z$ character (z-axis is taken as axis of rotation). Consequently, electron density is placed in the shrinking region of space between the two already negatively charged fluorine atoms. This situation contributes to the overall electronic instability of C_{2v} ClF_2 . In fact, fully occupying the $9a_1$ MO forces a species such as ClF_2^- to assume a more stable, linear geometry.

c) Finally, it should be noted that bending ClF_2 (for fixed Cl-F separation) monotonically increases the nuclear repulsion energy. This adds to the electronic instability of bent ClF_2 .

Evidently, the delocalization of the $3\pi_u$ LP's is sufficiently stabilizing so as to compensate for the instability brought about by the last two processes mentioned above. Hence, C_{2v} ClF_2 is more favorable energetically. Energy changes associated with the bending of linear ClF_2 may be seen in Table XIX. As bending of linear ClF_2 occurs, the electronic stability of bent ClF_2 arises from the greater lowering of the electronic energy relative to the increasing nuclear repulsion energy.

The Cl-F bond length calculated for the 2A_1 state of ClF_2 is 1.83Å (MBS, DZ and EXT basis sets) or 1.72Å (DZ + P basis). It is expected that the latter value is quite close to the true ClF_2 bond distance. This belief is, of course, based upon calculations of the $X^1\Sigma^+$ state of ClF performed with the DZ and DZ + P basis sets. Recall that these calculations produced Cl-F internuclear distances of 1.72Å (DZ basis) and 1.64Å (DZ + P basis), with the latter value being very near the experimental value of 1.63Å.

The Cl_3 radical is predicted to be bent (2A_1 electronic state) with a bond angle of 158.6° (DZ basis). One would expect Cl_3 to have a

molecular structure similar to ClF_2 since both radicals have 21 valence electrons. In fact, the slightly larger bond angle in Cl_3 is qualitatively⁴¹⁻⁴³ reasonable relative to ClF_2 . Since, in Cl_3 , the ligands are not as electronegative as fluorine, the bonding electrons are not drawn as far from the central atom as they are in ClF_2 . For this reason, the non-bonding electrons in Cl_3 cannot expand as much spatially. Hence, the bond angle in Cl_3 is slightly larger than in ClF_2 .

The Cl-Cl bond distance in Cl_3 was determined to be 2.33Å (DZ basis). This value is probably somewhat longer than the true value, since the DZ basis predicts a value of 2.15Å for the R_e of $X^1\Sigma_g^+ \text{Cl}_2$ as compared with the known experimental value¹ of 1.99Å.

Calculations performed on Cl_3 with polarization functions on the central atom yield a 2A_1 ground electronic state corresponding to a bent, symmetrical radical with a bond angle of 148.8°. This value of $\theta(\text{Cl}_3)$ is comparable to the bond angle determined for $^2A_1 \text{ClF}_2$. Thus, it would appear that the DZ + P basis employed for the Cl_3 calculations yields a quantitatively unreasonable value of $\theta(\text{Cl}_3)$. As stated above, one would predict Cl_3 to have a slightly larger bond angle than ClF_2 . The bond length, 2.25Å, determined with the DZ + P basis is (as expected) somewhat shorter than the distance calculated with the DZ basis set.

B. Pentatomic Molecules

Geometry predictions for the ClF_4^+ and ClF_4^- ions are given in Table VI, and for the ClF_4 radical in Table VII. Orbital energies for the ions and radical are listed in Table IX.

Calculations performed with the minimum and double zeta basis sets indicate that ClF_4^+ possesses a $^1\text{A}_1$ ground state corresponding to a square pyramidal geometry and an apex angle of 143.5° (DZ basis) or 148.4° (MBS). This C_{4v} structure is not consistent with the known C_{2v} structure²⁸ of the isoelectronic SF_4 molecule. However, calculations performed with the DZ + P basis yield a C_{2v} structure for ClF_4^+ , with axial and equatorial bond angles of 169.4° and 109.7° , respectively. These bond angles are very close to those determined experimentally²⁸ and theoretically⁴⁴ for SF_4 . The inability of the minimum basis set to predict a correct molecular structure for SF_4 has been revealed by Radom and Schaefer⁴⁴ and Guest *et al.*²⁹ While suitable for predicting the structure of the SF_4 molecule, the DZ basis is apparently not adequate for predicting the molecular structure or bond lengths of the ClF_4^+ molecule. Furthermore, it appears that in order to predict accurate bond lengths in SF_4 ⁴⁴ and the triatomic and pentatomic chlorine fluorides,^{45,46} one must include polarization functions on the central atom.^{47,48} The Cl-F bond length in the ClF_4^+ ion is calculated to be 1.78Å (MBS) or 1.76Å (DZ basis) for the C_{4v} structure. The axial and equatorial bond lengths determined for the C_{2v} ClF_4^+ ion are 1.625Å and 1.574Å, respectively. Thus, the theoretically determined bond lengths for C_{2v} ClF_4^+ are comparable to the experimental distances of 1.646Å and 1.545Å, in the SF_4 molecule.²⁸

VSEPR theory would picture ClF_4^+ with a shape such as

In such a structure, the electron pairs occupy as much space as possible while minimizing the number of approximately 90° bonding- non-bonding electron pair interactions.

The ClF_4^- ion is predicted to have a $^1A_{1g}$ ground electronic state corresponding to a square planar geometry (D_{4h} point group). This shape is consistent with the experimental finding of Christie and co-workers²⁵ and the theoretical determination of Guest, Hall and Hillier.²⁹ Logically, one might suppose that ClF_4^- would have a structure like that of the BrF_4^- ion⁴⁹ or the isoelectronic XeF_4 molecule,⁵⁰ which are known to have square planar shapes. The four equivalent Cl-F bonds in ClF_4^- are calculated to be 1.88Å in length with both the minimum and DZ basis sets. In this case, as in the case of the other chlorine fluorides, the bond distances are expected to decrease by 0.1Å - 0.15Å upon the addition of d polarization functions to the chlorine basis.

From a qualitative viewpoint, one could physically picture ClF_4^- as

where the two lone pairs of electrons, shown located on a line perpendicular to the molecular plane, occupy the $3a_{2u}$ and $3b_{1g}$ MO's in the symmetry notation of the D_{4h} point group.

The ClF_4 radical is predicted to be square planar (${}^2\text{A}_{1g}$ electronic state) using the minimum and double zeta basis sets, and square pyramidal (${}^2\text{A}_1$ electronic state) with an apex angle of 163.0° using the DZ + P basis set. A square planar structure for ClF_4 is consistent with the conclusion of Morton and Preston¹⁵ that ClF_4 should have a ${}^2\text{A}_{1g}$ ground electronic state and the theoretical prediction of a planar ClF_4 radical by Gregory.¹⁶

The conflict between the predictions of the DZ + P basis and the smaller basis sets warrants further discussion. Clearly, one should consider the equilibrium structure that any qualitative arguments might suggest for ClF_4 . One could picture ClF_4 as being formed by removing a single electron from the $6a_{1g}$ highest-occupied non-bonding orbital of planar ClF_4^- . It is expected that repulsion between the remaining lone pair of electrons and the four bonding pairs of electrons would tend to distort the fluorine ligands away from the molecular plane. This would allow the lone pair to occupy more space (delocalize) and thus increase the overall electronic stability of the radical. However, accompanying the formation of square pyramidal ClF_4 is an increase in nuclear repulsion energy and an increase in repulsion between four bonding pairs of electrons. Equally as important, a square pyramidal structure for ClF_4 would place the unpaired electron in an orbital possessing 26% chlorine $3p_z$ character (DZ + P calculation at predicted equilibrium geometry). This would imply that the unpaired electron was partly situated in a region of space surrounded by negatively charged fluorine atoms (similar to the case of ClF_2). Hence, qualitatively, one might conclude that the energy lowering associated with the delocalization of a single lone pair of electrons would not be sufficient to compensate for the energy increase brought about by the approach of four ligands to form a square pyramidal structure.

Shown in Table XIX are the energy changes associated with the bending of Cl-F bonds to form C_{4v} ClF_4 . Note that the increase in nuclear repulsion energy exceeds the decrease in electronic energy. Thus, C_{4v} ClF_4 is less stable relative to the planar structure.

Recall that in the case of ClF_2 , two lone pairs of electrons delocalize and only two bonding electron pairs repel each other as bending occurs. Thus, a bent structure is more reasonable, qualitatively, for ClF_2 than for ClF_4 .

A plausible alternative geometric arrangement for ClF_4 would be a C_{2v} structure, similar to that which the SF_4 and ClF_4^+ molecules possess. Associated with the formation of C_{2v} ClF_4 is the stabilizing effect of a single lone pair delocalization and the destabilizing effect of (essentially) two approaching ligands. It is unrealistic, of course, to assume that ClF_4 would benefit as greatly from a C_{2v} arrangement as does ClF_4^+ . This is due to the presence of the unpaired electron in ClF_4 . If ClF_4 were formed by adding an electron to ClF_4^+ , the electron would be placed in the $13a_1$ molecular orbital. A calculation of 2A_1 (C_{2v}) ClF_4 performed with $r_{ax} = r_{eq} = 1.69\text{\AA}$, $\theta_{ax} = 180^\circ$, and $\theta_{eq} = 163^\circ$, shows the $13a_1$ MO to possess 38% (DZ + P basis) chlorine $3p_z$ character. Again, the unpaired electron in C_{2v} ClF_4 is spatially situated between two approaching, negatively charged fluorine ligands. The bond distances and equatorial bond angle chosen for the assumed C_{2v} structure are those predicted with the DZ + P basis set for C_{4v} ClF_4 .

In any case, the three likely structures for ClF_4 , C_{2v} , C_{4v} and D_{4h} , are most probably very near one another in energy. Shown in Table XVII

are the energies calculated for three likely, geometrically distinct structures for ClF_4 . Note that the energy calculated for the C_{2v} structure with the DZ basis set is lower than that calculated for the C_{4v} structure. This lends credibility to the qualitative argument that the stability of $\text{C}_{2v} \text{ClF}_4$ should be greater than that of $\text{C}_{4v} \text{ClF}_4$.

4. Electronic Structure Considerations

Referring to Table VIII, it is seen that, except for the $\text{ClF}_2 4b_2$ orbital, the ordering via Koopman's Theorem of the occupied levels is identical for the radical and the ClF_2^+ ion. The ClF_2^- ion also has the same orbital ordering as ClF_2 , though the negative charge necessarily raises all of the energies. The closeness of the highest occupied $3\pi_u$ and $6\sigma_g$ orbitals supports the prediction that the first excited state is low-lying.

In the case of the ClF_4 radical, the $3b_{1g}$ and $6a_{1g}$ orbitals are very close together. It is also interesting to note that the level orderings for ClF_4 and ClF_4^- are identical and thus the notion of filling orbitals by the aufbauprinzip is justifiable.

Inspection of Tables X, XI and XII, reveals an interesting aspect of the Mulliken population analyses of the species ClF_2^+ , ClF_2 and ClF_2^- . The formation of ClF_2 from ClF_2^+ places 45.7% of the added charge on the fluorine atoms and 54.3% on the chlorine. Upon forming ClF_2^- from ClF_2 , 72.8% of the added negative charge is placed on the fluorine atoms while the remaining 27.2% is situated on chlorine. Thus, as one proceeds from ClF_2^+ to ClF_2 to ClF_2^- , the charge on chlorine increases by 31.6% ($\text{ClF}_2^+ \longrightarrow \text{ClF}_2$) and 18.4% ($\text{ClF}_2 \longrightarrow \text{ClF}_2^-$).

In the case of the pentatomic molecules, Tables XV and XVI show that as one proceeds from ClF_4 to ClF_4^- the charge on chlorine actually decreases by 0.3%.

The populations of the half-filled orbitals are of particular interest. For ClF_2 , the $9a_1$ orbital is seen, in Table XVIII, to be a roughly equal combination of Cl 3p and F 2p atomic functions. For ClF_4 , one may compare the results of Table XVIII with the conclusions of Morton and Preston from their EPR data. They note that there is considerable Cl 3s contribution to the orbital of the unpaired electron and estimate the amount to be between 17% and 50%. The present Mulliken analysis suggests that 11% of the $6a_{1g}$ orbital population is Cl 3s. This is in acceptable agreement with the experimental estimate in light of the imprecise nature of both the experimental and theoretical determinations.

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TABLE I

MINIMUM BASIS SET EXPONENTS AND CONTRACTION COEFFICIENTS

Center	Function	Exponent	Coefficient
Cl	1s	1408.2600	.0567524
		257.6940	.260141
		71.5903	.532846
		23.7602	.291625
	2s	91.0525	-.0622071
		19.7109	.000029768
		6.40877	.558855
		2.46139	.497767
		same as 2s	.0436843
	2p		.286379
			.583575
			.246313
	3s	4.06473	-.0852902
		1.11782	-.213207
		.439963	.592084
		.195804	.611558
	3p	same as 3s	-.0250495
			.16866
			.640955
			.277951
F	1s	390.337	.0567524
		71.4269	.260141
		19.8432	.532846
		6.58577	.291625
	2s	15.1086	-.0622071
		3.27068	.000029768
		1.06342	.558855
		.408425	.497767
		same as 2s	.0436843
	2p		.286379
			.583575
			.246313

TABLE II

DOUBLE ZETA BASIS SET EXPONENTS AND CONTRACTION COEFFICIENTS

Center	Function	Exponent	Coefficient
Cl	1s	105747.0	.000732
		15855.3	.005759
		3615.32	.029770
		1030.03	.118201
		339.691	.363632
		124.497	.582612
		124.497	.137213
	1s'	49.5143	.623311
		20.8138	.289946
		6.46497	1.0
	2s	2.52567	1.0
	2s'	.53814	1.0
	3s	.19356	1.0
	2p _x	587.622	.003003
		139.745	.023392
		44.7900	.104353
		16.5885	.284653
		2.71409	.325767
	2p _x '	6.60076	.447904
		.95008	1.0
	2p _y	same as 2p _x	1.0
	2p _y '	.95008	1.0
	3p _x	.35827	1.0
	3p _x '	.12499	1.0
F	1s	9994.79	.002017
		1506.03	.015295
		350.269	.07311
		104.053	.24642
		34.8432	.612593
		4.3688	.242489
		12.2164	1.0
	2s	1.2078	1.0
	2s'	.3634	1.0
	2p _x	44.3555	.020868
		10.0820	.130092
		2.9959	.396291
		.9383	.620368
	2p _x '	.2773	1.0
	2p _y	same as 2p _x	1.0
	2p _y '	.2733	1.0
F	2p _z	same as 2p _x	1.0
	2p _z '	.273300	1.0

TABLE III

EXTENDED BASIS SET (EXT) EXPONENTS AND CONTRACTION COEFFICIENTS. ONLY THE p-TYPE FUNCTIONS ARE LISTED. The s-TYPE FUNCTIONS ARE THE SAME AS THOSE LISTED FOR THE DOUBLE ZETA BASIS SET.

Center	Function	Exponent	Coefficient
Cl	$2p_x$	587.622	.0051830
		139.745	.0403730
		44.790	.1801100
		16.5885	.4913000
		2.71409	.5622610
	$2p'_x$	6.60076	1.0
	$2p_y$	same as $2p_x$	same as $2p_x$
	$2p'_y$	same as $2p'_x$	1.0
	$2p_z$	same as $2p_x$	same as $2p_x$
	$2p'_z$	same as $2p'_x$	1.0
	$3p_x$	.95008	
	$3p'_x$	.35827	1.0
	$3p''_x$	.12499	1.0
	$3p_y$	same as $3p_x$	same as $3p_x$
	$3p'_y$	same as $3p'_x$	1.0
	$3p''_y$	same as $3p''_x$	1.0
	$3p_z$	same as $3p_x$	same as $3p_x$
	$3p'_z$	same as $3p'_x$	1.0
	$3p''_z$	same as $3p''_x$	1.0
	$2p_x$	44.3555	.0420110
		10.0820	.2618990
		2.9959	.7976620
	$2p'_x$	.9383	1.0
	$2p''_x$	.2733	1.0
	$2p_y$	same as $2p_x$	same as $2p_x$
	$2p'_y$	same as $2p'_x$	1.0
	$2p''_y$	same as $2p''_x$	1.0
	$2p_z$	same as $2p_x$	same as $2p_x$
	$2p'_z$	same as $2p'_x$	1.0
	$2p''_z$	same as $2p''_x$	1.0

TABLE IV

GEOMETRY PREDICTIONS FOR ClF_2^+ and ClF_2^-

Molecule	Basis Set	Total Energy	Electronic State	$r(\text{Cl-F})$, Å	Bond Angle
ClF_2^+	MB	-654.0763	$1A_1$	1.72	98.2°
	DZ	-657.7177	$1A_1$	1.70	97.4°
ClF_2^-	MB	-654.2418	$1\Sigma_g^+$	1.87	linear
	DZ	-658.3305	$1\Sigma_g^+$	1.93	linear

TABLE V

GEOMETRY PREDICTIONS FOR THE ClF_2 and Cl_3 RADICALS

Molecule	Basis Set	Total Energy	Electronic State	$r(\text{Cl-F}), \text{\AA}$	Bond Angle
ClF_2	MB	-654.3749	$2\Sigma_g^+$	1.83	linear
	MB	-654.2353	$2\Pi_u$	1.79	linear
	DZ	-658.1439	$2A_1$	1.83	145.2°
	DZ	-658.1104	$2\Pi_u$	1.82	linear
	EXT	-658.1455	$2A_1$	1.83	145.2°
	DZ+P	-658.1868	$2A_1$	1.72	148.8°
	DZ	-1378.3505	$2A_1$	2.33	158.6°
	DZ+P	-1378.3661	$2A_1$	2.25	148.8°

TABLE VI

GEOMETRY PREDICTIONS FOR THE ClF_4^+ and ClF_4^- IONS

Molecule	Basis Set	Total Energy	Electronic State	$r(\text{Cl-F})$, Å	Bond Angle
ClF_4^+	MB	-851.1882	$^2A_1(C_{4v})$	1.78	148.4°
	DZ	-856.2678	$^2A_1(C_{4v})$	1.76	143.5°
	DZ+P	-856.4359	$^2A_1(C_{2v})$	1.625(r_{ax}) 1.574(r_{eq})	169.4°(θ_{ax}) 109.7°(θ_{eq})
ClF_4^-	MB	-851.3222	$^2A_{1g}$	1.88	planar
	DZ	-856.9899	$^2A_{1g}$	1.88	planar

TABLE VII

GEOMETRY PREDICTIONS FOR THE ClF_4 RADICAL

Basis Set	Total Energy	Electronic State	$r(\text{Cl-F}), \text{\AA}$	Bond Angle
MB	-851.4372	$^2A_{1g}$	1.82	planar
MB	-851.3418	$^2B_{1g}$	1.92	planar
DZ	-856.7535	$^2A_{1g}$	1.83	planar
DZ	-856.6734	$^2B_{1g}$	1.92	planar
DZ + P	-856.8705	$^2A_1(C_{4v})$	1.69	163.0°

TABLE VIII

ORBITAL ENERGIES IN A.U. FOR THE TRIATOMIC RADICALS AND IONS. RESULTS WERE OBTAINED FROM DOUBLE ZETA CALCULATIONS AT THE PREDICTED EQUILIBRIUM GEOMETRIES OF THE RESPECTIVE SPECIES.

ClF_2^+	ClF_2	ClF_2^-	Cl_3
$1a_1$ -105.417	$1a_1$ -105.029	$1\sigma_g$ -104.732	$1a_1$ -104.938
$2a_1$ -26.732	$2a_1$ -26.361	$2\sigma_g$ -25.994	$2a_1$ -104.908
$1b_2$ -26.732	$1b_2$ -26.361	$1\sigma_u$ -25.994	$1b_2$ -104.908
$3a_1$ -11.130	$3a_1$ -10.746	$3\sigma_g$ -10.450	$3a_1$ -10.660
$2b_2$ -8.596	$2b_2$ -8.214	$2\sigma_u$ -7.916	$4a_1$ -10.631
$4a_1$ -8.594	$4a_1$ -8.210	$1\pi_u$ -7.912	$2b_2$ -10.631
$1b_1$ -8.590	$1b_1$ -8.208	----	$3b_2$ -8.129
$5a_1$ -1.997	$5a_1$ -1.604	$4\sigma_g$ -1.256	$5a_1$ -8.124
$3b_2$ -1.951	$3b_2$ -1.593	$3\sigma_u$ -1.249	$1b_1$ -8.124
$6a_1$ -1.501	$6a_1$ -1.166	$5\sigma_g$ -0.884	$6a_1$ -8.100
$2b_1$ -1.084	$4b_2$ -0.725	$4\sigma_u$ -0.416	$4b_2$ -8.100
$7a_1$ -1.078	$2b_1$ -0.718	$2\pi_u$ -0.383	$7a_1$ -8.095
$4b_2$ -1.065	$7a_1$ -0.709	----	$2b_1$ -8.095
$1a_2$ -1.041	$1a_2$ -0.693	$1\pi_g$ -0.349	$1a_2$ -8.095
$5b_2$ -0.991	$5b_2$ -0.668	----	$5b_2$ -8.095
$8a_1$ -0.958	$8a_1$ -0.590	$3\pi_u$ -0.268	$8a_1$ -1.187
$3b_1$ -0.878	$3b_1$ -0.553	----	$6b_2$ -1.111
	$9a_1$ -0.538		$9a_1$ -1.045
			$7b_2$ -0.584
			$3b_1$ -0.564
			$10a_1$ -0.563
			$2a_2$ -0.509
			$8b_2$ -0.506
			$11a_1$ -0.478
			$4b_1$ -0.473
			$12a_1$ -0.449

TABLE IX

ORBITAL ENERGIES IN A.U. FOR THE PENTATOMIC MOLECULES. RESULTS WERE OBTAINED FROM THE DOUBLE ZETA CALCULATIONS AT THE PREDICTED EQUILIBRIUM GEOMETRIES OF THE RESPECTIVE SPECIES.

ClF_4^+	ClF_4	ClF_4^-
$1a_1$ -105.551	$1a_{1g}$ -105.009	$1a_{1g}$ -104.972
$1b_1$ -26.700	$1b_{1g}$ -26.390	$1b_{1g}$ -26.083
$1e$ -26.700	$1e_u$ -26.390	$1e_u$ -26.083
$2a_1$ -26.700	$2a_{1g}$ -26.390	$2a_{1g}$ -26.083
$3a_1$ -11.252	$3a_{1g}$ -10.916	$3a_{1g}$ -10.677
$2e$ -8.718	$2e_u$ -8.381	$2e_u$ -8.139
$4a_1$ -8.714	$1a_{2u}$ -8.376	$1a_{2u}$ -8.135
$5a_1$ -2.005	$4a_{1g}$ -1.674	$4a_{1g}$ -1.381
$3e$ -1.934	$3e_u$ -1.629	$3e_u$ -1.340
$2b_1$ -1.900	$2b_{1g}$ -1.608	$2b_{1g}$ -1.322
$6a_1$ -1.547	$5a_{1g}$ -1.258	$5a_{1g}$ -1.018
$4e$ -1.114	$4e_u$ -0.810	$4e_u$ -0.549
$7a_1$ -1.104	$2a_{2u}$ -0.799	$2a_{2u}$ -0.530
$1b_2$ -1.057	$1b_{2g}$ -0.748	$1b_{2g}$ -0.455
$5e$ -1.021	$1e_g$ -0.723	$1e_g$ -0.434
$3b_1$ -1.001	$1b_{2u}$ -0.714	$1b_{2u}$ -0.426
$6e$ -0.978	$5e_u$ -0.697	$5e_u$ -0.415
$1a_2$ -0.976	$1a_{2g}$ -0.690	$1a_{2g}$ -0.400
$8a_1$ -0.927	$3a_{2u}$ -0.618	$3a_{2u}$ -0.363
$4b_1$ -0.818	$3b_{1g}$ -0.575	$3b_{1g}$ -0.350
	$6a_{1g}$ -0.552	$6a_{1g}$ -0.274

TABLE X

MULLIKEN POPULATION ANALYSIS FOR ClF_2^+ . ALL VALUES TAKEN FROM THE DZ CALCULATION PERFORMED AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	Center	
	Cl	F (2 equiv.)
$1a_1$	2.0	0.0
2	0.0	1.0
3	2.0	0.0
4	2.0	0.0
5	0.244	0.878
6	1.580	0.210
7	0.315	0.843
8	0.864	0.568
$1a_2$	0.0	1.0
$1b_1$	2.0	0.0
2	0.423	0.789
3	1.579	0.210
$1b_2$	0.0	1.0
2	2.0	0.0
3	0.040	0.980
4	0.461	0.770
5	0.294	0.853
Total Charge	+1.202	-0.101

TABLE XI

MULLIKEN POPULATION ANALYSIS FOR ClF_2^- . ALL VALUES TAKEN FROM THE DZ CALCULATION PERFORMED AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	CENTER	
	Cl	F (2 equiv.)
$1\sigma_g$	2.0	0.0
2	0.0	1.0
3	2.0	0.0
4	0.113	0.943
5	1.804	0.098
6	0.095	0.952
$1\sigma_u$	0.0	1.0
2	2.0	0.0
3	0.057	0.972
4	0.524	0.738
$1\pi_u$	4.0	0.0
2	1.409	1.295
3	2.611	0.695
$1\pi_g$	0.0	2.0
Total Charge	+0.386	-0.693

TABLE XII

MULLIKEN POPULATION ANALYSIS FOR ClF_7 . ALL VALUES TAKEN FROM THE DZ CALCULATION PERFORMED AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	CENTER	
	Cl	F (2 equiv.)
$1a_1$	2.0	0.0
2	0.0	1.0
3	2.0	0.0
4	2.0	0.0
5	0.141	0.930
6	1.717	0.141
7	0.356	0.822
8	1.071	0.465
9	0.731	0.635
$1a_2$	0.0	1.0
$1b_1$	2.0	0.0
2	0.383	0.809
3	1.624	0.188
$1b_2$	0.0	1.0
2	2.0	0.0
3	0.047	0.976
4	0.472	0.764
5	0.166	0.917
Total Charge	+0.659	-0.329

TABLE XIII

MULLIKEN POPULATION ANALYSIS FOR Cl_3 . ALL VALUES TAKEN FROM THE DZ CALCULATION PERFORMED AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	CENTER	
	Cl	Cl (2 equiv.)
$1a_1$	2.0	0.0
2	0.0	1.0
3	2.0	0.0
4	0.0	1.0
5	2.0	0.0
6	0.0	1.0
7	0.0	1.0
8	1.269	0.365
9	0.687	0.656
10	1.308	0.346
11	0.602	0.699
12	0.139	0.931
$1a_2$	0.0	1.0
2	0.0	1.0
$1b_1$	2.0	0.0
2	0.0	1.0
3	1.294	0.353
4	0.708	0.646
$1b_2$	0.0	1.0
2	0.001	0.999
3	2.0	0.0
4	0.0	1.0
5	0.0	1.0
6	0.068	0.966
7	0.969	0.516
8	0.019	0.991
Total Charge	+0.006	-0.003

TABLE XIV

MULLIKEN POPULATION ANALYSIS FOR ClF_4^+ . ALL VALUES TAKEN FROM THE DZ + P CALCULATION PERFORMED AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	CENTER		
	Cl	F_{ax} (2 equiv.)	F_{eq} (2 equiv.)
$1a_1$	2.0	0.0	0.0
2	0.0	0.0	1.0
3	0.0	1.0	0.0
4	2.0	0.0	0.0
5	2.0	0.0	0.0
6	0.518	0.159	0.582
7	0.123	0.671	0.268
8	1.083	0.221	0.238
9	0.824	0.108	0.480
10	0.262	0.158	0.711
11	0.121	0.764	0.176
12	0.613	0.651	0.042
$1a_2$	0.058	0.189	0.782
2	0.012	0.789	0.205
$1b_1$	0.0	2.0	0.0
2	2.0	0.0	0.0
3	0.179	0.907	0.003
4	0.606	0.401	0.297
5	0.177	0.462	0.449
6	0.049	0.745	0.231
$1b_2$	0.0	0.0	2.0
2	2.0	0.0	0.0
3	0.185	0.002	0.907
4	0.738	0.076	0.555
5	0.043	0.007	0.967
6	0.040	0.884	0.096
Total Charge	+1.370	-0.192	+0.007

TABLE XV

MULLIKEN POPULATION ANALYSIS FOR ClF_4^- . ALL VALUES OBTAINED FROM THE DZ CALCULATION PERFORMED AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	CENTER	
	Cl	F (4 equiv.)
$1a_{1g}$	1.0	0.0
2	0.0	0.5
3	2.0	0.0
4	0.325	0.419
5	1.535	0.116
6	0.167	0.458
$1a_{2g}$	0.0	0.5
$1a_{2u}$	2.0	0.0
2	1.207	0.198
3	0.811	0.297
$1b_{1g}$	0.0	0.5
2	0.0	0.5
3	0.0	0.5
$1b_{2g}$	0.0	0.5
$1b_{2u}$	0.0	0.5
$1e_u$	0.0	1.0
2	4.0	0.0
3	0.139	0.965
4	1.396	0.651
5	0.079	0.980
$1e_g$	0.0	1.0
Total Charge	+1.339	-0.585

TABLE XVI

MULLIKEN POPULATION ANALYSIS FOR ClF_4 . ALL VALUES OBTAINED FROM THE DZ CALCULATION AT THE PREDICTED EQUILIBRIUM GEOMETRY.

Orbital	CENTER	
	Cl	F (4 equiv.)
$1a_{1g}$	2.0	0.0
2	0.0	0.5
3	2.0	0.0
4	0.328	0.418
5	1.486	0.128
6	0.207	0.448
$1a_{2g}$	0.0	0.5
$1a_{2u}$	2.0	0.0
2	0.894	0.276
3	1.119	0.220
$1b_{1g}$	0.0	0.5
2	0.0	0.5
3	0.0	0.5
$1b_{2g}$	0.0	0.5
$1b_{2u}$	0.0	0.5
$1e_u$	0.0	1.0
2	4.0	0.0
3	0.134	0.966
4	1.442	0.640
5	0.211	0.947
$1e_g$	0.0	1.0
Total Charge	+1.282	-0.321

TABLE XVII

ENERGIES FOR VARIOUS GEOMETRICALLY DISTINCT STRUCTURES FOR THE ClF_4 RADICAL

Basis Set	Electronic State	Total Energy	$r(\text{Cl-F}), \text{\AA}$	Apex Angle
DZ	${}^2A_{1g} (D_{4h})$	-856.7535*	1.83	planar
	${}^2A_1 (C_{4v})$	-856.7498*	1.83	160.0
	${}^2A_1 (C_{2v})$	-856.7514**	$r_{\text{ax}} = 1.83$ $r_{\text{eq}} = 1.83$	$\theta_{\text{ax}} = 180.0$ $\theta_{\text{eq}} = 160.0$
DZ + P	${}^2A_{1g} (D_{4h})$	-865.8559*	1.71	planar
	${}^2A_1 (C_{4v})$	-856.8705*	1.69	163.0
	${}^2A_1 (C_{2v})$	-856.8605**	$r_{\text{ax}} = 1.69$ $r_{\text{eq}} = 1.69$	$\theta_{\text{ax}} = 180.0$ $\theta_{\text{eq}} = 163.0$

* Calculated equilibrium geometry for this symmetry.

** Assumed geometry.

TABLE XVIII

MULLIKEN POPULATION ANALYSIS FOR THE SINGLY-OCCUPIED ORBITAL OF ClF_2 and ClF_4 . RESULTS WERE OBTAINED FROM THE DOUBLE ZETA CALCULATION AT THE PREDICTED EQUILIBRIUM GEOMETRIES.

		ClF_2	ClF_4
Cl	s	0.05	0.11
	p	0.31	0.00
	Total	+0.36	+0.11
F	s	0.00	0.00
	p	0.32	0.22
	Total	-0.32 (2 equiv.)	-0.22 (4 equiv.)

TABLE XIX

ENERGY CHANGES FOR THE BENDING OF C1-F BONDS IN THE ClF_2 and ClF_4 RADICALS,
ENERGIES ARE IN ATOMIC UNITS.

	ClF_2	ClF_4
ΔE_{elec}	-0.3846	-1.3819
ΔE_{nuc}	0.3780	1.3856
ΔE_{total}	-0.0066	0.0037

IV. THEORETICAL DIPOLE MOMENT FUNCTION OF THE $X^1\Sigma^+$ STATE OF HI

1. Introduction

Interest in the stable hydrogen halides, HX, where X = F, Cl, Br or I, dates back to the early part of this century.¹⁻⁶ The HX diatomic series has been studied extensively by experimental means^{7,8} and more recently by means of ab initio quantum mechanical methods.^{9,10}

Diatomic molecules such as the hydrogen halides have provided theoretical chemists with a great deal of useful information in the past 20 years. The results of studies conducted on diatomic molecules have provided an opportunity for chemists to establish the efficacy and reliability of their theoretical techniques. One of the first reliable ab initio molecular calculations¹¹ was carried out on the HF molecule. In the years following, HF has been one of the most thoroughly studied of the diatomic molecules.

The largest stable molecule in the HX series, HI, has received considerably less theoretical attention than HF. It has, however, been the subject of much experimental work.⁸ As early as 1894, HI was observed in a gas-phase reaction rate experiment.¹² This study prompted others^{13,14} to examine the kinetics of the now famous $H_2 + I_2 \longrightarrow HI + HI$ exchange reaction.

Work done more recently concerns the vibration-rotation spectrum (V-R) of HI. This spectrum was first measured successfully by Nielsen and Nielsen¹⁵ in 1935. Since then, a number of others¹⁶⁻²³ have also analyzed the V-R spectrum, placing special emphasis on the development of theoretical expressions for describing line intensities and the dipole moment function.²⁴ From these analyses, based upon increasingly accurate spectroscopic data,

it is clear that the V-R spectrum of HI is somewhat different from that of the other hydrogen halides. In 1962, Ameer and Benesch¹⁶ measured the V-R spectrum of HI and observed that the band intensity is "remarkably small compared with those of the other hydrogen halides". They also noted a striking dominance in intensity of the R over the P branch. Furthermore, they observed that the value of the linear term in the dipole moment function was negative. The dipole moment function is typically expressed as

$$\mu(R) = \sum_i M_i (R - R_e)^i \quad (1)$$

where

$$M_i = \frac{1}{i!} \frac{d^i \mu(R)}{dR^i} \quad (2)$$

Thus, a negative linear term in (1) indicates that the dipole moment of HI actually decreases with increasing internuclear separation.

In a more recent analysis,²¹ Tipping and Forbes also concluded that the maximum in $\mu(R)$ occurs at an internuclear separation much smaller than R_e . This is quite unlike the smaller hydrogen halides where the maximum in $\mu(R)$ occurs as a value of R which is greater than R_e .

The purpose of the present study is to seek theoretical confirmation of experimental results and gain an understanding of the difference between the dipole moment functions of the hydrogen halides.

The conceptual model utilized here is identical to that used by Lie in a theoretical study²⁵ of HF. Based upon Lie's results, it is expected that the present work should yield at least a qualitatively correct dipole moment function.

2. Electronic Wavefunction

The calculations performed in this study are of the multi-configuration self-consistent field²⁶ (MCSCF) type. Such a wavefunction is, of course, an approximate solution²⁷ to the non-relativistic electronic Schroedinger equation. The wavefunction consists of a linear combination of two configuration state functions²⁸ (CSF's)

$$\Psi = C_1\phi_1 + C_2\phi_2 \quad . \quad (3)$$

Each CSF is constructed from a set of orthonormal one-particle molecular spin-orbitals (MSO's). Each MSO is composed of a spatial part, $\phi(r)$, multiplied by a spin part, $\alpha(s)$ or $\beta(s)$. In this work, a fully occupied MSO would contain two electrons described by the same spatial function but different spin functions. The two configurations used to construct the MCSCF wavefunction are

$$\phi_1 = C \times 10\sigma^2 11\sigma^2 6\pi^4 \quad (4)$$

$$\phi_2 = C \times 10\sigma^2 12\sigma^2 6\pi^4 \quad (5)$$

where C denotes the core electron occupancy

$$1\sigma^2 2\sigma^2 \dots 9\sigma^2 1\pi^4 2\pi^4 \dots 5\pi^4 1\delta^4 2\delta^4 \dots \quad (6)$$

The first CSF is the Hartree-Fock configuration for the $X^1\Sigma^+$ state of HI. The second CSF permits the correct dissociation of the Hartree-Fock wavefunction to the atomic states $I(^2P_u)$ and $H(^2S_g)$. The second CSF also accounts for some of the most important effects due to electron correlation. The MCSCF 11σ and 12σ orbitals are basically bonding and anti-bonding combinations of the iodine $5p$ and hydrogen $1s$ atomic orbitals.

Each of the spatial functions, $\phi(R)$, was expanded in a basis of Slater type functions shown in Table I. The iodine basis was obtained largely from the SCF calculation²⁹ on I^- by Clementi and Roetti. To the iodine basis were added three sets of d functions to describe the polarization of the valence p -orbitals in the molecular framework. Polarization

functions are known to have importance in the calculation of reasonably accurate dipole moments.^{9,30,31} The hydrogen basis was taken from Liu's work³² on hydrogen halides and their anions. The total HI elementary basis consists of 14s, 12p, and 9d STF, or 35σ, 21π, and 9δ functions in the linear molecule notation.

During the course of the MCSCF calculation, both the mixing coefficients in (3) and the MO elementary function expansion coefficients were variationally determined.

The MCSCF wavefunction may be used to compute the expectation value of various operators for many useful molecular electronic properties.³³ For example, the expectation value of the dipole moment operator for a linear molecule is given by

$$\mu(R) = \langle z \rangle - \sum_i Z_i R_i \quad (7)$$

where $\langle z \rangle$ is the expectation value of the electronic charge with respect to a chosen coordinate origin (z axis is taken to be the internuclear axis), Z_i is the nuclear charge of the i^{th} center and R_i is the distance of the i^{th} center from the coordinate origin. For a neutral linear molecule, the dipole moment is independent of the coordinate origin.

3. Vibration-Rotation Theory

Inherent in the Born-Oppenheimer approximation³⁴ is the separation of electronic and nuclear motion. In this study, an approximate solution to the resulting equation for the electronic motion yields the wavefunction described in section 2. The motion of the nuclei in the potential field of the electrons is described by the nuclear wavefunction, $|v,J\rangle$ where v and J denote the vibrational and rotational quantum numbers, respectively. Such a function is determined by numerically integrating the radial Schroedinger equation

$$\left[\frac{-1}{2MR^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) + \frac{J(J+1)}{2MR^2} + E(R) \right] |v,J\rangle = E_{v,J} |v,J\rangle \quad (8)$$

where M is the nuclear reduced mass, $J(J+1)/2MR^2$ is the energy of a rigid rotator, $E(R)$ is the electronic potential energy in the field of the fixed nuclei and $E_{v,J}$ is the vibrational-rotational energy.

In addition to providing vibrational-rotational energy levels, which can be used to assess the quality of the electronic wavefunction, the integration of Eq. (8) yields the nuclear wavefunctions, which can be used to obtain vibrationally averaged expectation values of various operators.⁷ The averaged values may then be compared with known experimental quantities.

In matrix notation, the expectation value of the dipole moment operator in the state $|v,J\rangle$ is

$$\langle \mu \rangle_{v,J} = \langle v,J | \mu(R) | v,J \rangle .$$

This quantity is just a diagonal element of the dipole transition matrix

$$\langle v',J' | \mu(R) | v,J \rangle \quad v',J' = 0,1,2,\dots$$

$$J',J'' = 0,1,2,\dots$$

where v' and J' are the vibrational and rotational quantum numbers of the lower state. It is the square of the transition dipole matrix element which is proportional to the infrared line intensity observed in the V-R spectrum. The program used to integrate the radial Schrodinger equation was developed by K. Docken and J. Hinze. It is based on a method suggested by Cooley³⁵ and modified by Blatt.³⁶

4. Results and Discussion

The calculated total energies and dipole moments are listed in Table II and illustrated in Fig. 1. In Table III are listed the vibrationally averaged dipole moments and vibrational quanta. Calculated

and experimental values of the dipole moment function expansion coefficients, M_i , are listed in Table V.

The R_e and $E_{\min} = E(R_e)$ of the potential curve were determined by fitting the three lowest energy points to a quadratic polynomial. The dissociation energy, D_0 , was obtained by subtracting the computed zero-point vibrational energy from D_e (referring to Fig. 1, $D_e = 2.98$ eV). The calculated R_e , D_0 and μ_0 are presented in Table IV together with experimental results.

The calculated quanta agree with the experimental values²² to better than 100 cm^{-1} . The fact that the calculated E_{v0} are too small in magnitude is reflected by the shallowness of the potential curve. A calculation which yielded a deeper potential curve would undoubtedly raise the vibrational energy levels somewhat. The calculated R_e and D_0 of $3.10a_0$ and 2.81 eV are in good agreement with the experimental values of $3.04a_0$ ²² and 3.06 eV ,²² respectively. One could, of course, include more CSF's in the electronic wavefunction in order to obtain a more accurate value of D_0 . The calculated vibrationally averaged dipole moment is $0.665D$. This is in qualitative agreement with the experimental values of $\mu_0(\text{HI}) = 0.38D$ ³⁷ and $\mu_0(\text{DI}) = 0.445 \pm 0.02D$.³⁸ Since it was expected that the true dipole moment of HI should be nearly equal to that of DI, a vibrational-rotational analysis was performed on DI using the potential energy curve determined for HI. In this way, a vibrationally averaged dipole moment of $0.665D$ was obtained for DI.

The relative difference between the calculated and experimental values of μ_0 is large - 49% if $\mu_0(\text{DI}) = 0.445D$ is used as the true value.

This difference is generally expected when performing MCSCF calculations on a molecule with such a small permanent moment. In fact, Rosmus and Meyer³⁹ have shown that consideration of core-valence correlation effects is sometimes required if an error of 0.5D is to be avoided.

It is interesting to note that the HI SCF wavefunction predicts a value of R_e which is identical to the experimental value. The vibrationless dipole moment, μ_e , obtained with the SCF wavefunction at $R_e(\text{SCF}) = 3.04a_0$ is 0.665D.

In order to determine if the elementary basis set was deficient in terms of polarization functions, a set of $f(l=3)$ functions ($\zeta = 2.0$) was added to the initial basis, and calculations carried out at $R_e(\text{MCSCF}) = 3.10a_0$. The result was to lower the total SCF energy by 0.002 Hartree, while the vibrationless dipole moment decreased 1.6% from 0.666D to 0.655D. This value of $\mu_e(\text{HI})$ is identical to that obtained by Straub and McLean⁴⁰ using the SCF method and an extended polarization basis set for iodine and hydrogen. The MCSCF energy was also lowered 0.002 Hartree and the dipole moment, $\mu_e(\text{MCSCF})$, decreased 1.8% from 0.668D to 0.655D. At $R_e(\text{MCSCF}) = 3.10a_0$, partial optimization of the f function exponent lowered the MCSCF dipole moment an additional 0.3% to 0.653D. Hence, it is clear that any polarization effects which might be described by the 4f functions were satisfactorily described by the initially chosen 5d functions.

Tipping and Forbes²¹ have reported the coefficients in the expansion

$$\mu(R) = \sum_{i=0}^3 M_i x^i. \quad (9)$$

where

$$x = (R - R_e)/R_e \quad . \quad (10).$$

Accordingly, the dipole moment data in the region $R = 2.7a_0$ to $R = 3.4a_0$ were fit to a third degree polynomial in x using the least square method. The cubic polynomial reproduced all data points to better than 0.0001D. From an inspection of Table V it is evident that the agreement between the calculated and experimental M_1 is poor. However, this is expected considering the simple model employed and the neglect of relativistic effects.⁴¹

The calculated dipole moment function as shown in Fig. 1 decreases monotonically with increasing R for $1.8a_0 \leq R \leq 25a_0$. This is in agreement with the experimental finding¹⁶ that the dipole derivative of HI is negative at R_e , and the suggestion by Tipping and Forbes²¹ that the maximum in the dipole function of HI, unlike those of the other hydrogen halides, occurs at an internuclear separation smaller than R_e . Using the least squares method, the slope of the HI dipole curve in the region $2.7 \leq R \leq 3.4$ was determined to be $-0.0647D/\text{bohr}$. This may be contrasted with the value of $+1.692D/\text{Bohr}$ determined by Lie²⁵ for the $X^1\Sigma^+$ state of the much more polar HF molecule.

An explanation of the qualitative difference between the dipole moment function of HI and those of the smaller hydrogen halides may be found by considering the two diabatic electronic states arising from the

separated atom limits $H + X$ and $H^+ + X^-$. The potential curves of these states exhibit minima due to covalent bonding and electrostatic attraction, respectively. Relative to the appropriate asymptotic limit, ionic bonds are stronger than covalent bonds. Thus, the possibility exists that the diabatic ionic potential curve may cross the diabatic covalent potential curve at some point, and become the lowest electronic state at smaller R . This may occur in spite of the fact that the $H^+ + X^-$ asymptote lies ~ 10 eV above the $H + X$ asymptote. Such a crossing is favored by a small asymptotic energy difference between the two states and a strong ionic attraction.

Since the asymptotic energy difference is nearly the same for all hydrogen halides, within 0.6 eV, it is only necessary to consider the strength of the ionic bond. The ionic bond energy may be roughly approximated by $-1/R_X$, where R_X is the ionic radius of the halogen atom, X . From this it is seen that the crossing is most likely to occur for HF and least likely for HI. In cases where the two diabatic states do cross, the adiabatic ground state electronic wavefunction is primarily ionic in character at smaller values of R and becomes increasingly more covalent as R increases. The dipole moment function for such an electronic state would begin at zero and remain small for large R , rise rapidly near the crossing point reaching a maximum and fall off almost as a linear function of R . Furthermore, for ionic bonds the maximum in the dipole moment function occurs to the right of R_0 . In a higher order approximation, where the two diabatic electronic wavefunctions are allowed to mix, the crossing between the ionic and covalent curves is avoided and

the adiabatic ground state potential curve is always connected to the $H + X$ asymptote. In cases where the two diabatic curves do not cross, the adiabatic ground state electronic wavefunction is predominantly covalent in character, but acquires increasing ionic character with decreasing R . The dipole moment function corresponding to such an electronic state begins at zero and rises slowly with increasing R , reaching a maximum when the nuclei are in close proximity to one another. Therefore, the trend seen in the dipole moment functions of hydrogen halides results from decreasing ionic character and increasing covalent character with increasing size of the halogen atom. The shape of the dipole moment curve indicates that the HI bond is primarily covalent. This is also reflected by the very small $\mu_0(\text{HI})$ as compared with the μ_0 of the other hydrogen halides.

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TABLE I
BASIS SET OF SLATER-TYPE FUNCTIONS

Center	Function Type	Orbital Exponents
I	1s	54.538, 37.211
	2s	27.730, 24.215
	3s	18.174, 12.177
	4s	7.345, 5.538
	5s	3.283, 1.969, 1.011
	2p	34.379, 22.878
	3p	13.261, 11.1694
	4p	7.111, 4.940
	5p	3.002, 1.776, 1.027
	3d	19.305, 11.264
	4d	6.847, 4.271, 2.454
	5d	3.002, 1.776, 1.027
H	1s	1.94, 1.00, 0.52
	2p	1.94, 1.00, 0.52
	3d	1.00

TABLE II

TOTAL ENERGIES AND DIPOLE MOMENTS FOR THE $X^1\Sigma^+$ STATE OF HI.

$R(a_0)$	E (Hartree)	μ (Debye)
1.80	-6918.00585	0.8317
2.00	-6918.24994	0.7890
2.20	-6918.39996	0.7468
2.30	-6918.45079	0.7316
2.40	-6918.48977	0.7232
2.50	-6918.51901	0.7120
2.55	-6918.53063	0.7069
2.70	-6918.55589	0.6940
2.80	-6918.56632	0.6866
3.00	-6918.57622	0.6739
3.10	-6918.57718	0.6675
3.20	-6918.57623	0.6607
3.40	-6918.57030	0.6449
3.70	-6918.55577	0.6136
4.00	-6918.53904	0.5707
4.30	-6918.52295	0.5148
4.70	-6918.50480	0.4242
5.25	-6918.48745	0.2900
6.00	-6918.47555	0.1484
7.00	-6918.47049	0.0611
8.00	-6918.46938	0.0318
9.00	-6918.46914	0.0196
10.00	-6918.46909	0.0129
20.00	-6918.46906	0.0007
25.00	-6918.46905	0.0004

TABLE III

VIBRATIONALLY AVERAGED DIPOLE MOMENTS, IN DEBYE, AND
VIBRATIONAL QUANTA, IN cm^{-1} , for $\text{HI}(X^1\Sigma^+)$

v	μ_v	$\Delta G_{v+1/2}(\text{calc})$	$\Delta G_{v+1/2}(\text{exper.})^a$
0	0.655	2165.0	2229.5
1	0.658	2078.8	2149.7
2	0.650	1991.6	2068.8
3	0.641	1903.0	1986.7
4	0.630	1812.6	--
5	0.617	1720.2	--
6	0.601	1624.7	--
7	0.583	1525.8	--
8	0.562	1421.8	--
9	0.536	--	--

^aREF [22]

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF R_e ,
 D_0 and μ_0 FOR $HI(X^1\Sigma^+)$

Calculation	R_e (bohr)	D_0 (eV)	μ_0 (debye) ^a
SCF	3.04	--	(0.665) ^b
MCSCF	3.10	2.81	0.665
Experiment	3.04 ^c	3.06 ^c	0.445±0.02 ^d

^aThe calculated dipole moment is in the direction I^-H^+ for all R.

^bThis is the vibrationless dipole moment, μ_e , evaluated by interpolation at R_e (SCF) = 3.04 bohrs.

^cREF [22]

^dREF [38]

TABLE V

DIPOLE MOMENT FUNCTION COEFFICIENTS. VALUES ARE IN DEBYE.

Coefficient	Calculated Value	Empirical value ^a
	R_e (MCSCF) = 3.04 bohr	R_e = 3.04 bohr
M_0	0.671	0.445 ± 0.02
M_1	-0.192	-0.0765 ± 0.0029
M_2	-0.0800	0.496 ± 0.040
M_3	-1.56	-1.94 ± 0.20

^aREF [21]

FIGURE CAPTION

- Fig. 1 Potential energy and dipole moment curves for the $X^1\Sigma^+$ -states of HI and HF. Potential energy points for HF taken from G. C. Lie and E. Clementi, J. Chem. Phys. 60, 1275 (1974). Dipole moment points taken from G. C. Lie, J. Chem. Phys. 60, 2991 (1974). Arrows indicate R_e of potential curves.

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V. CONFIGURATION INTERACTION CALCULATIONS OF THE
 $^2\Sigma^+$ F + H₂ POTENTIAL ENERGY SURFACE

1. Introduction

The reaction, depicted schematically in Fig. 1,

has been the subject of considerable experimental and theoretical research. The reaction (1), is representative of a majority of chemical processes, which take place on an asymmetric potential energy surface. As the best understood reaction of its type, it has been studied with a variety of experimental techniques. Infrared chemiluminescence,¹⁻³ chemical laser⁴⁻⁹ and molecular beam techniques¹⁰⁻¹² have been used to determine energy and angular distributions of the reaction products. Rate constants and activation energies have been determined by mass spectrometry^{13,14} and hot-atom experiments.^{15,16}

The $^2\Sigma^+$ ground electronic potential energy surface of the F + H₂ system has been the subject of extensive trajectory studies¹⁷⁻³⁴ in addition to semi-classical and exact quantum scattering studies.³⁵⁻³⁷ Ab initio computations have also been performed to produce ground³⁸⁻⁴¹ and excited⁴⁰ ($^2\Pi$) electronic potential energy surfaces. Additional ab initio work focused on spin-orbit^{41,42} and non-adiabatic⁴¹⁻⁴⁴ effects in the reaction of F with H₂. Self consistent field^{43,44} and configuration

interaction³⁸ calculations of the lowest lying $2A'$ non-linear potential energy surface have been carried out. The results³⁸ showed the non-linear surface to have a significantly larger barrier to reaction than the linear surface.

Previous ab initio studies³⁸⁻⁴⁰ of the $F + H_2$ potential surface, as informative as they have been, have not satisfactorily examined the qualitative effects on the potential surface of changing basic aspects of the wavefunction. In order to fully understand, theoretically, the nature of chemical reactions in general, it is crucial that a reaction of this type be well characterized by a complete theoretical treatment. It is, therefore, the purpose of the present study to thoroughly examine the $F + H_2$ reaction from a theoretical standpoint with the use of the configuration interaction (CI) method.⁴⁶ The results will, hopefully provide an indication as to what is required to produce a "chemically accurate" potential surface for use in dynamical research.

2. Elementary Basis Sets

In Table I is the largest basis set employed in this study, consisting of six s, four p, three d and one f Slater-type functions (STF) on fluorine and three s, two p and one d STF on hydrogen. Thus, the total number of functions in this basis set was 12s, 8p, 5d and 1f STF or 26σ , 14π , 6δ and 1ϕ orbitals in linear molecule notation. Orbital exponents for the fluorine basis were determined by Liu during previous research⁴⁷ on HF. The hydrogen basis orbital exponents were determined by performing full configuration interaction calculations of the $X^1\Sigma_g^+$ state of H_2 and varying the exponents until successive total energy differences were less than 5×10^{-5} a.u.

In addition to the above, three other basis sets were employed in the present study. The first, shown in Table II, was the basis set used by Cade and Huo in a near Hartree-Fock study⁴⁸ of the $X^1\Sigma^+$ state of HF. This set contained five s, four p, two d and one f STF on fluorine and three s, two p and one d STF on hydrogen for a total of 12s, 8p, 4d and 1f STF. The corresponding number of linear orbitals for this basis was 20σ and 10π . In Table III is the third basis set, referred to as a small Slater basis, and consisting of four s, three p and one d STF on fluorine and two s and one p STF on hydrogen. The total number of STF composing this basis set was 8s, 5p and 1d or 14σ , 6π and 1 δ orbitals. The exponents for the small basis were taken from the work of Bagus and Gilbert.⁴⁹

The fourth, Gaussian basis set, will be described in a later section concerning the vibrational analysis of HF_2 .

3. Types of CI Wavefunctions

Initial computations were performed with the large Slater basis set shown in Table I. Configurations were generated using the method of McLean and Liu.⁵⁰ Consequently, all following discussions related to the generation of n-particle spaces will make use of the terminology presented by McLean and Liu in their paper⁵⁰ on the subject.

From the basis of one-particle functions, totaling 26σ , 14π , 6δ , and 1ϕ orbitals, three configuration state functions (CSF's) shown in Table IV, were chosen to compose the zeroth order (reference) subspace. In the first, Hartree-Fock configuration, the 1σ , 2σ , 3σ , and 4σ orbitals are roughly the fluorine 1s, 2s, H_2 bonding and fluorine $2p_z$ orbitals, respectively. The 1π orbitals is, then, roughly the fluorine $2p_x$ and $2p_y$

orbitals. Configurations (2) and (3) were included in the zeroth order subspace in order to accurately describe the dissociation of the H_2 molecule as the H_2 bond is broken during the reaction with fluorine atoms. Thus, the 5σ orbital in configurations (2) and (3) is approximately the H_2 antibonding orbital. In addition, the configurations (2) and (3) account for some of the important valence correlation effects which result from the interaction of F with H_2 . An MCSCF calculation⁵¹ which included the CSF's (1), (2) and (3) was performed to produce the initial set of internal and external orbitals. It should be noted that the configuration

$$\phi_4 = 1\sigma^2 2\sigma^2 3\sigma 4\sigma 5\sigma 1\pi^4 \quad (3\sigma, 5\sigma) \quad 1\Sigma^+$$

is redundant and may be formed⁵² from a linear combination of configurations (1) and (2). Hence, this configuration was omitted from the MCSCF calculation and the zeroth order subspace. The internal orbital set was chosen to be the 1σ , 2σ , 3σ , 4σ , 5σ and 1π orbitals, while the remaining 21σ , 13π , 6δ and 1ϕ molecular orbitals constituted the external subspace. The n-particle space included all interacting singly and doubly substituted CSF's relative to the set of zeroth order configurations with two restrictions; 1) the 1σ orbital was constrained to be doubly occupied in all CSF's, and 2) the 2σ orbital was constrained to be doubly occupied for all excitations into the external subspace. With these restrictions, a total of 8790 CSF's were produced. Of the 8790 CSF's generated, 6874 were selected by the following procedure.

A zeroth order wavefunction was variationally determined by solving the equation

$$H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

where $\psi^{(0)}$ was composed of the 24 CSF's produced by holding the 1 σ orbital doubly occupied and effecting all permissible excitations within the internal subspace. Using $\psi^{(0)}$, the Rayleigh-Schroedinger first order perturbed wavefunction

$$\begin{aligned}\psi &= \psi^{(0)} + \psi^{(1)} \\ &= \sum_{I=1}^{24} \psi_I^{(0)} + \sum_{J \neq I} \frac{H_{JI}}{E_J^{(0)} - E_I^{(0)}}\end{aligned}$$

where

$$H_{JI} = \langle \phi_J | H | \phi_I \rangle$$

was constructed. The index J runs over all remaining configurations (25 - 8790) constituting the n-particle space. The first order reduced density matrix, γ , formed from the perturbed wavefunction, was diagonalized and the first natural orbitals (NO's) produced from the one-particle basis of molecular orbitals. Based upon the occupation numbers of the natural orbitals, a new 6874 CSF n-particle space was produced from an internal orbital set composed of the MCSCF orbitals occupied in configuration (1) and an external orbital set consisting of the 5-22 σ , 2-12 π , 1-6 δ , and 1 ϕ natural orbitals obtained with the perturbed wavefunction. The CI wavefunction spanning this n-particle space was then used to locate the saddle point on the potential surface. In addition, the asymptotic equilibrium internuclear distances of the reactant H₂ and product HF were determined. The results are shown in Tables V and VI. The predicted classical barrier height of 3.93 kcal/mole obtained by subtracting the reactants energy, E(F + H₂), from the calculated saddle point energy is quite large in comparison with the value of 1.7 kcal/mole estimated experimentally⁵³ for the reaction activation energy, E_a. The quantity referred to as ΔD_e is given by

$$\Delta D_e = E(F + H_2) - E(HF + H)$$

ΔD_e was evaluated with the reactant and product internuclear separations, R(H₂) and R(HF), fixed at 1.40a₀ and 1.7328a₀, respectively. A value of $\Delta D_e = 32.6$ kcal/mole was calculated which is excellent agreement with

the corresponding experimental value of 31.5 ± 0.5 kcal/mole. As can be seen from Fig. 1 one may readily obtain $\Delta D_e(\text{exp})$ by adding the zero-point energies⁵⁴ of H_2 and HF to the respective spectroscopic dissociation energies,^{55,56} and evaluating the expression

$$\Delta D_e = D_e(\text{HF}) - D_e(\text{H}_2) \quad .$$

The predicted saddle point geometry, $r^\ddagger(\text{F-H}) = 2.79a_0$ and $r^\ddagger(\text{H-H}) = 1.47a_0$, indicates that the $\text{F} + \text{H}_2$ reaction is predominantly repulsive in nature. That is, the reaction barrier and, hence, the reaction energy release occur as the fluorine atom approaches H_2 . Recall that an attractive surface would release the reaction energy as the products (HF and H) separated from one another.

In the asymptotic regions of the potential energy surface, the equilibrium internuclear separations of the reactant, H_2 , and product, HF , were determined to be $1.395a_0$ and $1.723a_0$, respectively. These values, obtained by fitting 3 data points to a quadratic polynomial, are in excellent agreement with the known diatomic distances of $1.4011a_0$ ⁵⁵ and $1.7328a_0$.⁵⁷

Shown in Table VII are the results of perturbation-CI calculations performed with the large Slater basis modified to describe F^- . This modification had very little effect as may be seen. The barrier height and ΔD_e were determined to be 3.99 kcal/mole and 32.6 kcal/mole, respectively. Thus, the need to describe a diffuse fluorine atom seems

somewhat unlikely. However, the effects of adding a diffuse polarization function to the fluorine basis will be discussed in a later section.

Also shown in Tables V and VII are the results of calculations performed with the large Slater basis, which made use of a CI wavefunction including all interacting singly and doubly substituted CSF's relative to a single (Hartree-Fock) reference configuration shown in Table IV. In this case, only the 1σ orbital was constrained to be doubly occupied in all CSF's. The internal and external orbital subspaces, consisting of the orbital sets $\{1-4\sigma, 1\pi\}$ and $\{5-26\sigma, 2-14\pi, 1-6\delta, 1\phi\}$, respectively, were generated at each of three points on the potential surface by performing restricted SCF calculations. Two sets of CI calculations were then carried out at the chosen points. The first set of calculations was performed with the 2σ orbital held doubly occupied in all CSF's generated by promoting electrons into the external subspace. The resulting CI wavefunction was used to determine a barrier height and ΔD_e of 5.47 kcal/mole and 30.8 kcal/mole, respectively. The barrier height is substantially greater than that determined with the 3 reference CSF wavefunctions. Thus, one would conclude that the use of a single reference CSF results in the omission of important correlation effects at the saddle point. The calculated ΔD_e is in excellent agreement with the experimental value, differing by only -0.7 kcal/mole from the latter.

The second set of calculations performed using 1 reference CSF included 2σ correlation. In this case, the CI wavefunction was used to determine a barrier height and ΔD_e of 6.03 kcal/mole and 28.7 kcal/mole, respectively. As might have been expected, the inclusion of 2σ correlation increased the barrier height somewhat (0.56 kcal/mole). This

stems from the fact that the fluorine atoms benefits more from 2σ correlation as a reactant than at the saddle point. Thus, the energy of the reactants, $E(F + H_2)$, is lowered by more than that of the triatomic species, $E(F-H-H)$. Hence, the barrier increases. The ΔD_e decreased by 2.1 kcal/mole. This, too, is not unexpected for reasons similar to those stated for the change in barrier height. However, in the case of ΔD_e , the inclusion of 2σ correlation lowered the energy of the reactants, $E(F + H_2)$, by more than that of the products, $E(HF + H)$. Hence, as may be deduced from Fig. 1, the net result was to decrease ΔD_e .

The saddle point was also located using the 5966 CSF wavefunction. The interatomic distances were found to be $r(F-H) = 2.50a_0$ and $r(H-H) = 1.48a_0$. Thus, the saddle point occurs somewhat later on the 5966 CSF surface than on the 6874 CSF surface. Further, the saddle point geometry found using 1 reference CSF and including 2σ correlation is not comparable to that determined by Bender *et al.*³⁹ Using a 1 reference configuration, first order wavefunction, Bender and co-workers located the saddle point at $r(F-H) = 2.90a_0$ and $r(H-H) = 1.45a_0$, corresponding to a barrier height of 1.66 kcal/mole. The latter researchers also calculated a value of 34.4 kcal/mole for ΔD_e .

Finally, internuclear separations determined for the H_2 and HF molecules in the asymptotic regions of the potential surface computed with the 5966 CSF wavefunction were $1.408a_0$ and $1.735a_0$, respectively.

For investigative purposes, additional calculations were carried out with the Cade and Huo basis set shown in Table II, and the small Slater basis shown in Table III. Using the Cade and Huo basis set, a

3954 CSF n-particle space was generated in a fashion identical to that used to generate the 8790 CSF space described previously. The internal and external subspaces chosen for the 3954 CSF CI calculation consisted of the orbital sets $\{1-5\sigma, 1\pi\}$ and $\{6-20\sigma, 2-10\pi\}$, respectively. Again, calculations were performed at three points on the potential surface. The results are shown in Table VII. The calculated value of the barrier height was identical to that determined with the perturbation-CI wavefunction modified to describe F^- . The calculated ΔD_e , 26.5 kcal/mole, differs from the experimental value by -5.0 kcal/mole; this results, primarily, from the inability of the hydrogen basis set to properly describe two separated hydrogen atoms (2S_g electronic state). In the present case, the hydrogen basis indicates a D_e for the hydrogen molecule of 114.1 kcal/mole as compared to the known value⁵⁵ of 109.48 kcal/mole. Thus, it is easily seen that the net result of this basis set deficiency would be to lower the energy of the reactants by more than that of the products and subsequently decrease the magnitude of ΔD_e . One would tend to conclude that the original large Slater basis was satisfactory for describing the nature of the individual atomic species. Furthermore, the results obtained with the Cade and Huo basis show that the use of the perturbation technique to generate the n-particle space was justified.

Several interesting results were obtained with the small Slater basis. These are shown in Table VII. Three n-particle spaces, which included all interacting CSF's produced by single and double excitations from one, three and seven CSF zeroth order subspaces, shown in Table IV were utilized in this case. For calculations performed with a single reference CSF, the internal and external subspaces consisted of the

orbital sets $\{1-4\sigma, 1\pi\}$ and $\{5-14\sigma, 2-6\pi, 1\delta\}$, respectively. Energies were computed at three points on the potential surface. Referring to Table VII, it is readily seen that the size of the zeroth order subspace has a pronounced effect on the magnitude of the calculated reaction barrier height. Calculations including 2σ correlation show that, as one proceeds from 1 to 3 to 7 reference CSF's, the barrier height decreases from 5.22 kcal/mole to 3.55 kcal/mole to 2.95 kcal/mole. Thus, it is clear that important correlation effects are omitted using one reference CSF. Further, it is evident that additional, important correlation effects are accounted for by the inclusion of seven configurations in the zeroth order subspace. The omission of 2σ correlation is indicated to have little effect on the calculated value of the barrier height, but a relatively great effect on the calculated value of ΔD_e . Note that the change in the barrier height is much less than that obtained with the large Slater basis, 1 reference CSF wavefunction. With the large Slater basis, the omission of 2σ correlation lowered the barrier by 9.3%. Whereas, using the small Slater basis, 1 reference CSF wavefunction, the omission of 2σ correlation lowered the barrier by only 0.76%. A similar discrepancy was observed for the calculated values of ΔD_e . The omission of 2σ correlation increases the ΔD_e by 7.3% using the large Slater basis, while ΔD_e increases by only 2.69% with the small basis set. Thus, it is clear that the small basis is inadequate for quantitatively determining energy differences brought about by changing important aspects of the CI differences.

A calculation was performed with a $3s$ function ($\zeta = 0.6$) added to the fluorine basis. In this case, the small basis, 1 reference CSF wavefunction was used to calculate a barrier and ΔD_e of 3.42 kcal/mole

and 28.6 kcal/mole, respectively. Again, it is seen that it is not necessary to describe a diffuse fluorine atom in order to calculate meaningful potential surface features.

Based upon the qualitative results of the calculations performed with the small Slater basis, it was concluded that two aspects of the CI wavefunction must be considered in order to properly describe the $F + H_2$ potential surface. Firstly, if accurate values of ΔD_e are desired, it is necessary to include 2σ correlation in the wavefunction. Secondly, important correlation effects at the saddle point must be included in the wavefunction by the use of a seven configuration zeroth order subspace.

The most complete CI wavefunction utilized in the present study spanned a 12,509 CSF space. In this case, the n-particle space included all interacting CSF's produced by effecting single and double excitations from two zeroth order subspaces into two external subspaces. Both zeroth order subspaces spanned a one-particle space composed of the $1-5\sigma$ and 1π orbitals. All single and double excitations were effected from the zeroth order CSF

$$1\sigma^2 \ 2\sigma^2 \ 3\sigma^2 \ 4\sigma^1 \ 5\sigma^0 \ 1\pi^4$$

into the full external orbital set, $6-26\sigma$, $2-14\pi$, $1-6\delta$, 1ϕ . In addition, all interacting CSF's were generated by exciting 1 and 2 electrons from seven reference CSF's, shown in Table IV, into the truncated external orbital set consisting of the orbitals $6-15\sigma$, $2-9\pi$, $1-3\delta$, and 1ϕ . The

internal and external orbital sets of one-particle functions consisted of the first natural orbitals produced from a CI calculation performed with the 5966 CSF wavefunction. As before, three points were run on the potential surface. The results are shown in Table V. The barrier height, 3.71 kcal/mole, is comparable to the value of 3.93 kcal/mole obtained with the 6874 CSF wavefunction. The saddle point location on this surface, corresponding to the geometry $r(\text{F-H}) = 2.78a_0$ and $r(\text{H-H}) = 1.46a_0$, is nearly identical to that of the surface produced with the 6874 CSF perturbation-CI wavefunction. The calculated ΔD_e , 29.3 kcal/mole, is somewhat less than the value obtained with the perturbation-CI wavefunction. However, as shown in Table VIII, the former is just the seven reference CSF limit. The calculated asymptotic equilibrium internuclear separations in this case were $1.406a_0$ and $1.732a_0$, for H_2 and HF , respectively.

Table IX shows the results of orbital deletions on the potential surface. The results, obtained by subtracting the energies, $E(12,509 \text{ CSF})$ and $E(5966 \text{ CSF})$, show that the one-particle basis is complete with respect to higher-than-double excitations. Hence, no additional significant change in the potential surface features would be observed by including more orbitals in the truncated external subspace.

4. Vibrational Analysis

In order to properly determine the activation energy, E_a , and exothermicity, ΔD_0 , of the $\text{F} + \text{H}_2$ reaction, it is necessary to account for the zero-point vibrational energy of the reactants, products and triatomic saddle point species. Referring to Fig. 1, one may readily note that it is only necessary to add the zero-point energies of H_2 and HF

to the calculated reactant and product energies, respectively, to determine the exothermicity. However, to obtain E_a , one must perform a vibrational analysis of the triatomic species, F-H-H, at the predicted saddle point. This was accomplished in the present work by assuming a general quadratic valence force field⁵⁸ and solving Lagrange's equations of motion. Expressing the potential, V, as

$$V = \frac{1}{2} \sum_{i,j=1} F_{ij} S_i S_j$$

Then the F_{ij} is the force constant associated with the centers i and j, while S_i and S_j are internal coordinates of the i^{th} and j^{th} centers. In the present study, the F_{ij} were determined by least square fitting potential surface data to a 10 term Taylor series expansion about the saddle point. Included in the expansion were all quadratic terms and cross products plus the products $S_1^0 S_2^3$ and $S_1^3 S_2^0$. The calculated F_{ij} are shown in Table X, together with the vibrational frequencies corresponding to the symmetric and asymmetric stretching modes of the activated complex. Using a linear potential surface, one may determine the vibrational energy at the saddle point for the stretching mode corresponding to the real frequency. However, the energy associated with the doubly degenerate bending mode must be arrived at by performing calculations of non-linear F-H-H at the predicted saddle point. For this purpose, a calculation of the F + H₂ potential surface was carried out with a double zeta plus

polarization Gaussian basis set consisting of four s, two p and one d STF on fluorine and two s and one p STF on hydrogen contracted according to Dunning.⁵⁹ With this basis, totalling 20a' and 10a'' orbitals in C_s symmetry notation, a total of 2939 CSF's were generated. To generate the n-particle space the 1a' orbital was held doubly occupied in all CSF's and all interacting singly and doubly substituted configurations relative to a single reference (Hartree-Fock) configuration were retained. As shown in Table V, the predicted saddle point location, $r(\text{F-H}) = 2.47a_0$ and $r(\text{H-H}) = 1.50a_0$, is quite close to that predicted with the large basis, 1 reference 5966 CSF wavefunction. The calculated barrier, 8.87 kcal/mole, is also comparable in magnitude to that obtained with the large basis 5966 CSF wavefunction. The ΔD_e , 24.3 kcal/mole, determined for this surface is significantly smaller than the known value 31.5 ± 0.5 kcal/mole. This trend is, again, similar to that observed using the large Slater basis.

The calculated bending force constant was obtained by fitting three non-linear potential points to a three term expansion in the even powers, 0, 2 and 4 of the displacement angle,

$$\alpha = 180 - \theta(\text{F-H-H}).$$

The force constant and vibrational frequency determined in this way are shown in Table X. Using the stretching frequency determined with the large basis, 12,509 CSF wavefunction, and the bending frequency calculated with the Gaussian basis wavefunction, the zero-point energy at the saddle

point on the linear surface was calculated as 5.23 kcal/mole. As shown in Table XI, the activation energy, E_a , was subsequently determined to be 2.74 kcal/mole. This is in reasonable agreement with the estimated experimental value of 1.7 kcal/mole. The reaction exothermicity, ΔD_o , obtained by including diatomic zero-point corrections in the expression for ΔD_e , was calculated to be 30.0 kcal/mole. This quantity differs by -1.5 kcal/mole from the known value.

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TABLE I
LARGE BASIS SET OF SLATER-TYPE FUNCTIONS

Center	Function Type	Orbital Exponents
F	1s	14.413, 8.513
	2s	6.444, 4.902, 2.706, 1.86
	2p	8.636, 3.911, 2.030, 1.266
	3d	3.6, 1.3
	4d	3.6
	4f	4.0
H	1s	1.35, 1.0, 0.8
	2p	1.8, 1.0
	3d	2.4

TABLE II

BASIS SET OF SLATER-TYPE FUNCTIONS TAKEN FROM THE WORK OF CADE AND HUO.

Center	Function Type	Orbital Exponents
F	1s	14.10946, 7.94374
	2s	3.25633, 1.93465
	2p _σ	8.97251, 4.27843, 2.37325, 1.40701
	2p _π	9.29742, 4.26145, 2.32912, 1.35836
	3s	9.9254
	3d _σ	3.36796, 1.83539
	3d _π	2.1338
	4f _σ	2.7001
	4f	2.79365
H	1s	2.46048, 1.37269
	2s	2.46147
	2p _σ	2.92262
	2p _π	1.77056
	3d _π	3.32049

TABLE III
SMALL BASIS SET OF SLATER-TYPE FUNCTIONS

Center	Function Type	Orbital Exponents
F	1s	10.5136, 7.71588
	2s	3.12022, 1.93329
	2p	5.219, 2.599, 1.154
	3d	2.0
H	1s	1.4, 1.0
	2p	1.8

TABLE IV
CONFIGURATIONS INCLUDED IN THE ONE, THREE AND SEVEN CSF ZEROth ORDER SUBSPACES

1	Number of CSF's		7
	3		
$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^4$	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^4$		$1\sigma^2 2\sigma^2 2\sigma^2 4\sigma 1\pi^4$
	$1\sigma^2 2\sigma^2 5\sigma^2 4\sigma 1\pi^4$		$1\sigma^2 2\sigma^2 4\sigma^2 3\sigma 1\pi^4$
	$1\sigma^2 2\sigma^2 3\sigma \ 4\sigma \ 5\sigma 1\pi^4$	$(3\sigma, 5\sigma) \ ^3\Sigma^+$	$1\sigma^2 2\sigma^2 5\sigma^2 4\sigma 1\pi^4$
			$1\sigma^2 2\sigma^2 5\sigma^2 3\sigma 1\pi^4$
			$1\sigma^2 2\sigma^2 4\sigma^2 5\sigma 1\pi^4$
			$1\sigma^2 2\sigma^2 3\sigma^2 5\sigma 1\pi^4$
			$1\sigma^2 2\sigma^2 3\sigma \ 4\sigma \ 5\sigma 1\pi^4$
			$(3\sigma, 5\sigma) \ ^3\Sigma^+$

TABLE V

FEATURES OF THE $F+H_2$ POTENTIAL ENERGY SURFACE DETERMINED WITH VARIOUS CI WAVEFUNCTIONS

Basis	# ref. CSF	# frozen orbitals	Total # CSF	$E(HF+H)^\dagger$ hartrees	Saddle Point		Barrier Height* kcal/mole	ΔD_e^{**} kcal/mole
					$r(F-H), a_0$	$r(H-H), a_0$		
Gaussian	1	1	2939	-100.7314	2.47	1.50	8.87	24.3
Large	1	1	5966	-100.8432	2.50	1.48	7.12	28.7
Large	3	2	6874	-100.7645	2.79	1.47	3.93	32.6
Large	7	2	12,509	-100.8464	2.78	1.46	3.71	29.3

* Barrier height determined relative to $R(H_2)_{\text{reactant}}$ fixed at $1.40a_0$.

** Exothermicity determined with $R(H_2)_{\text{reactant}}$ and $R(HF)_{\text{product}}$ fixed at $1.40a_0$ and $1.7328a_0$, respectively.

$^\dagger R(HF) = 1.7328 a_0$.

TABLE VI
CALCULATED ASYMPTOTIC POTENTIAL ENERGY SURFACE INTERNUCLEAR SEPARATIONS.
EXPERIMENTAL VALUES ARE IN PARENTHESES.

Basis Set	# ref. CSF	Total # CSF	Frozen Orbitals	$r(\text{H}_2), a_0$	$r(\text{HF}), a_0$
Large Slater	1	5966	1	1.408(1.4011)	1.735(1.7328)
Large Slater	3	6874	2	1.395	1.723
Large Slater	7	12,509	1	1.406	1.732

TABLE VII

FEATURES OF *ab initio* POTENTIAL ENERGY SURFACES FOR THE REACTION $F + H_2 \longrightarrow HF + H$. SADDLE POINT GEOMETRY IS THAT DETERMINED WITH THE LARGE SLATER BASIS PERTURBATION- CI WAVEFUNCTION.

	# ref. CSF	# frozen orbitals	Total # CSF	E(HF+H) hartree	Saddle Point		Barrier Height kcal/mole	ΔD_e kcal/mole
					$r(F-H), a_0$	$r(H-H), a_0$		
Cade-Huo F(5s4p2d1f) H(3s1p1d)	3	2	3954	-100.7013	2.79	1.47	3.99	26.5
Small basis	1	2	588	-100.7040	2.79	1.47	5.22	28.2
Small basis	1	1	1081	-100.7532	2.79	1.47	5.26	27.5
Small basis	3	2	1598	-100.7075	2.79	1.47	3.55	29.6
Small basis	3	1	3279	-100.7564	2.79	1.47	3.64	28.3
Small basis	7	2	2142	-100.7075	2.79	1.47	2.95	29.6
Small basis	7	1	4691	-100.7564	2.79	1.47	2.97	28.3
Large Basis	1	2	2344	-100.7608	2.79	1.47	5.47	30.8
Large Basis	1	1	5966	-100.8432	2.79	1.47	6.03	28.7
Large Basis Modified to describe F^-	3	2	6874(8790)	-100.7630	2.79	1.47	3.99	32.6
Large Basis	7	2	6450	-100.7660	2.79	1.47	2.41	33.2
Large Basis	7	1	12,509	-100.8464	2.79	1.47	3.73	29.3

TABLE VIII

DETERMINATION OF ΔD_e IN THE LIMIT OF SEVEN REFERENCE CONFIGURATIONS.
ENERGIES TAKEN FROM CALCULATIONS PERFORMED WITH THE LARGE SLATER
BASIS SET.

Calculation	Species	Frozen Orbitals	Total Energy	ΔD_e , kcal/mole
Diatomic	F + H ₂	2	-100.7147	31.2
	HF + H	2	-100.7645	
	F + H ₂	1	-100.8022	28.0
	HF + H	1	-100.8468	
Triatomic	F + H ₂	2	-100.7131	33.2
	HF + H	2	-100.7660	
	F + H ₂	1	-100.7996	29.3
	HF + H	1	-100.8464	

TABLE IX

CONVERGENCE DATA FOR THE 12,509 CSF CI CALCULATION

ΔE evaluated at $r(\text{F-H}) = 2.79_a$ and $r(\text{H-H}) = 1.47$

One-Particle Basis				ΔE , a.u.*
σ	π	δ	ϕ	
13	1			0.00093
15	1			0.00099
18	1			0.00099
22	1			0.0010
26	1			0.0010
26	7			0.0044
26	9			0.0044
26	12			0.0044
26	14			0.0044
26	14	1		0.0049
26	14	3		0.0051
26	14	6		0.0051
26	14	6	1	0.0051

* $\Delta E = (12,509 \text{ CSF}) - E(5966 \text{ CSF})$

TABLE X
VIBRATIONAL ANALYSES AT LINEAR SADDLE POINT GEOMETRIES

Basis Set	# ref CSF	Saddle Point		Force Constants md/A			Vibrational-1 Frequencies, cm	
		r(F-H), a ₀	r(H-H), a ₀	F ₁₁	F ₂₂	F ₁₂	ν ₁	ν ₂
Gaussian *	1	2.47	1.50	-0.9128	3.853	1.555	2890	1493 i
Large	1	2.50	1.48	-1.098	4.220	1.435	3101	1435 i
Large	3	2.79	1.47	-1.165	4.509	1.843	3116	1672 i
Large	1 + 7	2.78	1.46	-0.6254	4.132	1.226	3157	1134 i

* $F_{\alpha} = 0.00670 \text{ md/A-rad}^2$; $\nu_{\alpha} = 252 \text{ cm}^{-1}$

TABLE XI

ZERO-POINT ENERGY CONTRIBUTIONS AND ACTIVATION ENERGY AT THE
SADDLE POINT DETERMINED WITH THE 12,509 CSF WAVEFUNCTION.

Energy Contribution	Energy, kcal/mole
Symmetric Stretch	4.51
Bend (doubly degenerate)	2 x +0.36
Total zero-point	5.23
Classical barrier height	+ 3.71
H ₂ zero-point energy*	- 6.20
Activation Energy, E _a	2.74

* Ref. [54]

FIGURE CAPTION

Fig. 1 Energy diagram for the $F + H_2$ reaction.

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VI. THE WEAK ATTRACTION BETWEEN WATER AND METHANE

1. Introduction

The present paper concerns the simplest hydrophobic¹ interaction, the interaction between a single water molecule and a single methane molecule. In his review Tanford¹ concludes that the hydrocarbon tail of an amphiphile should have thermodynamic properties similar to those of a hydrocarbon molecule in water solution. Since it is clear that the water-methane interaction potential plays a crucial role in determining the latter thermodynamic properties, the relation between the present study and the hydrophobic effect is indirectly established. For physical chemists, the $\text{H}_2\text{O}-\text{CH}_4$ interaction is of inherent interest, and would probably be estimated to be intermediate between a van der Waals attraction (e.g., Ne-Ne, ~ 0.09 kcal/mole²) and a true hydrogen bond (e.g., $\text{H}_2\text{O}-\text{H}$, ~ 5 kcal/mole³).

Despite the large number of hydrogen bonded systems for which ab initio electronic structure studies have been undertaken,⁴ only one such calculation for the $\text{H}_2\text{O}-\text{CH}_4$ system has been reported previously. This calculation, by Lathan et al.,⁵ was carried out as part of a comprehensive study of the equilibrium geometries of all molecules of the form H_mABH_n , where A and B are first row atoms C, N, O, and F. They performed self-consistent field computations with a minimum basis set of Slater functions, each expanded as a linear combination of three Gaussian functions. Lathan et al. predict the equilibrium structure, seen in Figure 1, to be bound by 0.8 kcal/mole relative to separated CH_4 and H_2O .

The relative dearth of $\text{H}_2\text{O}-\text{CH}_4$ theoretical studies has in part been motivated by some skepticism as to the validity of the Hartree-Fock

approximation for describing potential surfaces of this type. The qualitative suitability of single configuration wave functions for the descriptions of systems such as $\text{H}_2\text{O}-\text{H}_2\text{O}$ and $\text{HF}-\text{HF}$ seems well established.⁴ However, the failure of Hartree-Fock to predict any attraction at all for He-He, Ne-Ne, and Ar-Ar, is equally well established.⁶ It should be noted that for the He-He⁷ and Ne-Ne⁸ systems, studies explicitly including correlation effects have yielded qualitatively correct potential energy curves. Thus, the inherent inability of the Hartree-Fock model to describe dispersion forces does raise serious questions as to the suitability of this model for describing the $\text{CH}_4-\text{H}_2\text{O}$ interaction. The same questions have been noted by Losonczy, Moskowitz, and Stillinger,⁹ whose $\text{H}_2\text{O}-\text{Ne}$ Hartree-Fock calculations predict a binding energy of only 0.17 kcal/mole. On the other hand, if Pople's prediction⁵ of an 0.8 kcal/mole attraction is qualitatively correct, then the dispersion contribution (which we can guess to be ~ 0.1 kcal/mole from the Ne-Ne molecular beam results²) will be relatively unimportant.

The purpose of the present study, then, is to carefully study the $\text{H}_2\text{O}-\text{CH}_4$ interaction at the self-consistent-field level of theory using several different basis sets. A variety of different approaches of H_2O to CH_4 have been considered. Finally, a number of calculations are reported for the $\text{H}_2\text{O}-\text{CH}_4-\text{H}_2\text{O}$ system.

2. Comparison of Basis Sets

Four different basis sets of contracted Gaussian functions⁷ have been used in the present study:

- A. Minimum Basis. $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ Slater functions on carbon and oxygen were each expanded as a linear combination of four Gaussian functions.¹⁰ Orbital exponents were taken from Clementi and Raimondi.¹¹ Similarly, a $1s$ Slater function on hydrogen (orbital exponent 1.2) was fit as a linear combination of four Gaussians. Although this basis set yields significantly lower total energies than the STO-3G set of Lathan et al.,⁵ both are minimum basis sets and one expects qualitatively similar geometry predictions and energy differences.
- B. Double Zeta Basis. Twice as large as the minimum basis, this is Dunning's C, O(4s 2p), H(2s) contraction¹² of Huzinga's C, O(9s 5p), H(4s) primitive Gaussian basis sets.¹³
- C. This third basis set is identical to the double zeta set above, except that the primitive (5p) set is more flexibly contracted, to (3p).
- D. Double Zeta Plus d. To basis B, is added a set (d_{xx} , d_{yy} , d_{zz} , d_{xy} , d_{xz} , d_{yz}) of d-like functions to carbon ($\alpha = 0.75$) and oxygen ($\alpha = 0.8$).

To allow a comparison of the different basis sets, the simplest linear O - H - C arrangement, designated geometry A and seen in Figure 2, was studied first. The H_2O and CH_4 geometries are held fixed at their experimental values:^{14,15} $r(OH) = 1.809$ bohrs = 0.957 Å, $\theta(HOH) = 104.52^\circ$; and for tetrahedral CH_4 , $r(CH) = 2.067$ bohrs = 1.094 Å, $\theta(HCH) = 109.47^\circ$.

The results of this comparison are seen in Table I. There it is seen that the minimum basis set yields an H_2O-CH_4 bond energy of 1.81 kcal/mole, large enough to be considered a true hydrogen bond. This result

is surprisingly different from the minimum basis work of Lathan et al.,⁵ who found only 0.8 kcal/mole of binding. The source of this difference probably lies not with the fact that the MBS functions are expressed in terms of a 4 Gaussian expansion (as opposed to their 3 Gaussians), but rather with their use of orbital exponents optimal for molecules, not atoms. In any case, it is seen clearly that all minimum basis sets are not alike. Note, however, that the Lathan calculation predicted a C-O separation of 3.27 Å, only 0.16 Å longer than obtained with the present minimum basis.

The double zeta calculation yields a much longer C-O distance (3.85 Å) and much weaker attractive energy (0.49 kcal/mole). Basis set C yields an almost identical result, indicating clearly that the additional flexibility in the carbon and oxygen 2p functions is unnecessary.

The final calculation, that using the double zeta plus d basis, yields an even longer C-O bond distance (4.01 Å) and smaller attraction (0.34 kcal/mole). This same trend, toward smaller binding energy with increasing basis set size, occurs for the water dimer.⁷ In fact the near Hartree-Fock calculations of Popkie, Kistenmacher, and Clementi³ yield a hydrogen bond energy which is almost certainly less than the correct (unknown) value. Thus it appears that the correlation energy will be of the order of one kcal/mole greater for the water dimer than for two separated H₂O molecules. In light of these facts, it is by no means clear whether the double zeta or double zeta plus d results are closer to reality. It is believed that the minimum basis results are unreliable.

Given the uncertainties involved, the double zeta basis was used in the remaining phases of the study. In addition to the obvious economic advantages, there would seem to be a substantial probability that the basis set and correlation errors would cancel with respect to this frame of reference.

3. The Different Orientations of Approach

In addition to geometry A, four other approaches are considered, B, C, D, and E, depicted in Figure 2. These results are summarized in Table II and Figure 7, both of which indicate that approaches B, C, and E are repulsive in nature. This is not particularly surprising when one considers the many statements in the literature¹ concerning the lack of affinity between hydrocarbons and water.

A few qualitative comments can be made concerning the repulsive interactions B, C, and E. First, the fact that C is by far the most repulsive is understood in terms of the highly unfavorable H-H interaction. That is, in a simple picture, the H atoms in H_2O and CH_4 are positively charged, and these effective charges repel via Coulomb's law. The similarity of the mildly repulsive interactions B and E is readily understood by comparison of Figures 2b and 2e. These two conformations share the undesirable feature of placing a large number of atoms in the same region of physical space.

The second most attractive conformation is geometry D, with binding energy 0.17 kcal/mole and C-O equilibrium separation 4.16 Å. Like geometry A, this conformation involves a linear O - H - C arrangement, a result consistent with the many earlier theoretical studies of hydrogen bonded systems.⁴

As well as the basic arrangements A-E, rotations (about the various C-O axes) of one molecule relative to the other have been considered.

For geometries A and D, these rotations were done at the equilibrium geometries, i.e., $r_e(\text{CO})$. The barrier to rotation for geometry A is so small, less than 0.0001 kcal/mole, as to lie in the noise level of the present calculations. For geometry D, however, the dependence on angle of rotation was significant. If we let $\gamma=0^\circ$ correspond to the geometry seen in Figure 2d, then the following additional results were found:

$\gamma = 0^\circ$, 0.172 kcal/mole; $\gamma = 10^\circ$, 0.173 kcal/mole; $\gamma = 20^\circ$, 0.176 kcal/mole; $\gamma = 40^\circ$, 0.188 kcal/mole; $\gamma = 60^\circ$, 0.201 kcal/mole; $\gamma = 75^\circ$, 0.208 kcal/mole; and $\gamma = 90^\circ$, 0.211 kcal/mole. Thus it is seen that the binding energy goes up monotonically from 0.17 to 0.21 kcal/mole as γ goes from 0° to 90° . Energies for other values of γ are related by symmetry to those in the range 0 - 90° . Note finally that the $\gamma = 90^\circ$ geometry allows the left most (in Fig. 2d) H atom to "avoid" the two nearest methane hydrogens.

Although geometry B yields a completely repulsive interaction potential, by rotating the H_2O molecule by 90° , a weak attraction of 0.05 kcal/mole was found. This rotated geometry is referred to as B' in Table II. As is reasonable, this more favorable conformation corresponds to the maximum separation of water protons from the two nearest methane hydrogens.

A. Approach of a Second Water Molecule

In a dilute solution, each hydrocarbon molecule will be surrounded by several water molecules. Clearly a purely ab initio attack on a completely realistic liquid is not practical. However, by assuming a

pairwise additive potential, it is possible to simulate the liquid via molecular dynamics.^{16,17} Thus it is of interest to investigate the potential surfaces involving more than two molecules and check the deviations from the pairwise model. For the water trimer such calculations have already been reported.^{18,19}

The equilibrium geometry of $\text{CH}_4(\text{H}_2\text{O})_2$ will of course be that of a methane molecule loosely bound to the water dimer. However, given the present interest in the hydrophobic effect, this is not the conformation of primary concern here. Rather, a $\text{CH}_4(\text{H}_2\text{O})_2$ structure with two O - H - C hydrophobic interactions is considered. Since geometry A yielded the lowest $\text{CH}_4\text{-H}_2\text{O}$ energy, this dimer structure was fixed at $r_1(\text{CO}) = 3.85 \text{ \AA}$. Then a second water molecule was brought up in an analogous manner. Note that when the second C-O distance, $r_2(\text{CO})$, is 3.85 Å the three molecule complex has C_{2v} point group symmetry.

A rather surprising result was found at this latter geometry, namely that the energy with respect to separated $\text{CH}_4 + \text{H}_2\text{O} + \text{H}_2\text{O}$ is only -0.132 kcal/mole. That is, when one $\text{CH}_4\text{-H}_2\text{O}$ dimer is fixed at its equilibrium geometry, the second $\text{CH}_4\text{-H}_2\text{O}$ interaction becomes repulsive. Other results obtained with $r_1(\text{CO}) = 3.85 \text{ \AA}$ were the following:
 $r_2(\text{CO}) = 4.0 \text{ \AA}$, $E = -0.175 \text{ kcal/mole}$; $r_2(\text{CO}) = 5.0 \text{ \AA}$, $E = -0.157 \text{ kcal/mole}$;
 and $r_2(\text{CO}) = 7.5 \text{ \AA}$, $E = -0.305 \text{ kcal/mole}$. All these results are seen to lie above the -0.494 kcal/mole result obtained for $r_1(\text{CO}) = 3.85 \text{ \AA}$,
 $r_2(\text{CO}) = \infty$.

In a pairwise additive picture, the potential energy of the $r_1 = r_2 = 3.85 \text{ \AA}$ structure is $2 \cdot (-0.494 \text{ kcal/mole})$ plus the potential energy of two H_2O molecules as they remain when the CH_4 is removed to infinity.

It is seen, then, that this $\text{H}_2\text{O}-\text{H}_2\text{O}$ interaction should be repulsive by 0.856 kcal/mole to satisfy pairwise additivity. This $\text{H}_2\text{O}-\text{H}_2\text{O}$ calculation carried out at $r(\text{O}-\text{O}) = 6.287 \text{ \AA}$, indicated an energy of 0.695 kcal/mole relative to separated $\text{H}_2\text{O} + \text{H}_2\text{O}$. Thus it is seen that the assumption of pairwise additivity is qualitatively reasonable in this case.

4. Population Analyses

Table III shows Mulliken populations²⁰ for infinitely separated $\text{H}_2\text{O} + \text{CH}_4$, for the equilibrium positions of geometries A and D, and for $\text{CH}_4(\text{H}_2\text{O})_2$ with $r_1(\text{CO}) = r_2(\text{CO}) = 3.85 \text{ \AA}$. Although one is correctly hesitant to assign any significance to the precise values of these atomic populations, it is at least hoped that population comparisons will be chemically meaningful.

First note that, consistent with any simple picture of electronegativity, the H atoms in H_2O are substantially more positively charged than those in methane. For geometry A, the bridging H atom in the linear $\text{O} \cdots \text{H}-\text{C}$ structure is labeled H_1 in Table III. At the equilibrium of geometry A, the positive charge on this bridging hydrogen is significantly increased with respect to that of isolated methane. This loss of electron density is counteracted by increases at the neighboring O and C atoms. Thus, the expected picture $\overset{\delta-}{\text{O}} - - - \overset{\delta+}{\text{H}} - - - \overset{\delta-}{\text{C}}$ is confirmed.

For structure D, the H atom in the $\text{O}-\text{H} \cdots \text{C}$ bridge is labeled H_2 in Table III. Again an increase in positive charge, 0.004 here, at the bridging hydrogen is seen. Although the 0.004 magnitude is miniscule in an absolute sense, the fact that it is a difference, along with the weak nature of the interaction, allows one to conclude, as before,

that electron density flows to some degree to the neighboring more electronegative O and C atoms.

The Mulliken populations for the trimer show that the two water molecules have very similar charge distributions to isolated H_2O . However, these waters significantly distort the central methane charge distribution. The C atoms are more negatively charged by 0.054 electron, and a very large difference in the two sets of equivalent H atoms develops. The bridging H's (H_1 and H_2 on methane in Table III) become 0.046 electron more positively charged than in CH_4 , while the terminal hydrogens are more negatively charged, by 0.021 electron. It is concluded that these Mulliken populations present a picture of the electronic charge distribution which is consistent with both chemical intuition and the ab initio predictions made here.

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TABLE I

SUMMARY OF CALCULATIONS USING VARIOUS BASIS SETS FOR $\text{H}_2\text{O}-\text{CH}_4$. RESULTS IN THIS TABLE REFER ONLY TO GEOMETRY A, DETERMINED TO LIE LOWER ENERGETICALLY THAN THE OTHER GEOMETRIES INVESTIGATED. SEE TEXT FOR A FURTHER DESCRIPTION OF THE DIFFERENT BASIS SETS.

Basis	$R_e(\text{C-O}), \text{\AA}$	E (hartree)	Binding Energy (kcal/mole)
A. Minimum Basis	3.11	-115.27652	1.810
B. Double Zeta C,O (9s 5p/4s 2p) H (4s/2s)	3.85	-116.19539	0.494
C. C,O (9s 5p/4s 3p) H (4s/2s)	3.88	-116.19663	0.485
D. Double Zeta Plus d C,O (9s 5p 1d/4s 2p 1d) H (4s/2s)	4.01	-116.23600	0.339

TABLE II

EQUILIBRIUM BOND DISTANCES AND RELATIVE ENERGIES OF THE DIFFERENT $\text{H}_2\text{O}-\text{CH}_4$ GEOMETRICAL APPROACHES. ALL CALCULATIONS WERE CARRIED OUT WITH THE DOUBLE ZETA BASIS SET DESCRIBED IN THE TEXT.

Geometry	R_e (C-O), Å	Binding Energy (kcal/mole)
A	3.85	0.494
B	Repulsive Interaction	
B'	4.22	0.050
C	Repulsive Interaction	
D	4.16	0.172
E	Repulsive Interaction	

TABLE III.

MULLIKEN POPULATIONS FOR THE WATER-METHANE INTERACTION.

	POPULATIONS								
	H ₂ O			CH ₄					
	H ₁	H ₂	O	H ₁	H ₂	H ₃	H ₄	C	
Separated Molecules	0.613	0.613	8.773	0.807	0.807	0.807	0.807	6.772	
Equilibrium Geometry A	0.610	0.610	8.776	0.752	0.817	0.818	0.818	6.798	
Equilibrium Geometry D	0.615	0.609	8.778	0.825	0.807	0.798	0.798	6.771	
CH ₄ (H ₂ O) ₂	0.612	0.612	8.774	0.761	0.761	0.828	0.828	6.826	

FIGURE CAPTIONS

- Fig. 1 Qualitative view of the equilibrium geometry predicted by Lathan et al.⁵ using a minimum basis set. Note that the O---H separation is not to scale, being 3.27 Å in reality, as opposed to ~ 1 Å for the intramolecular OH and CH distances in water and methane.
- Fig. 2 Schematic view of the various approaches of water to methane.
- Fig. 3 Potential curves for the one-dimensional interactions depicted in Fig. 2. Note that the results obtained from geometry E are not plotted, as this potential curve is quite similar to curve B. For example, at $R(\text{C-O}) = 4.0$ and 5.0 Å, curve E lies 0.09 kcal/mole below curve B.

Pople equilibrium geometry

XBL 745-3043

Geometry A

XBL 745-3042

Geometry B

XBL 745-3039

Geometry C

XBL 745-3040

Geometry D

XBL 745-3041

Geometry E

-151-

XBL745 - 3348