

Pseudopotential SCF-MO studies of hypervalent compounds. I. XeF₂ and XeF₄

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The (*ab initio*) effective potential theory developed by Ewig *et al.* has been applied to a series of hypervalent compounds with a view to elucidating the anomalous properties of several of the higher fluorides of xenon and iodine. In this initial paper the development of a minimal basis set substantially better than an STO-4G atom-optimized set is described. Calculations carried out on XeF₂ and XeF₄ give valence orbital energies in fair agreement with those obtained with the more flexible, all-electron SCF-MO calculations by Basch *et al.* Equilibrium structures of XeF₂ and XeF₄ provided by the effective potential calculations possess the correct symmetries. Bond lengths, although too long by 0.09 Å, correctly reproduce the contraction observed experimentally upon fluorination of XeF₂. Calculated bending and stretch-stretch interaction force constants are in pleasing agreement with experiment, as is the stretching anharmonicity. Stretching frequencies evaluated at the experimental bond length, however, are 25% high. Overall, the ability of the present treatment to give a reasonable account of the structures and force fields of XeF₂ and XeF₄ justifies its application to the higher fluorides where interpretations of observations are more speculative.

I. INTRODUCTION

After their discovery about two decades ago,¹ the rare-gas compounds soon lost their aura of strangeness and were quickly assimilated into the mainstream of chemistry. Xenon halides, for example, were found to resemble hypervalent halides of other elements, such as iodine, whose higher valence had long been taken for granted. As information about physical properties accumulated, however, puzzling aspects of some hypervalent molecules were noticed, not only among xenon compounds, but also among those of iodine. The anomalous properties of xenon hexafluoride, interpreted in quite different ways by different workers, have not yet been resolved unequivocally.²⁻⁴ Iodine heptafluoride, closely analogous to xenon hexafluoride in the number of its central-atom valence electrons, was originally believed to be a simple pentagonal bipyramid. Subsequent studies have cast doubt on this.^{5,6} Experimental difficulties encountered in characterizing the higher fluorides stem, at least in part, from the rather large amplitude internal motions of the molecules. Because of these, the compounds tend neither to exhibit simple, readily interpretable spectra nor, in the case of IF₇, to yield well-ordered molecular crystals for x-ray studies. The compounds are also corrosive and troublesome to handle.

Such experimental difficulties make these intriguing substances attractive candidates for theoretical investigations and, indeed, the lower fluorides have been the subject of a number of *ab initio* quantum calculations. Unfortunately, it has been impractical, heretofore, to carry out *ab initio* calculations of the structures and force fields of the higher fluorides because of their numerous electrons and their many internal coordinates. Recent advances in theory have changed the picture dramatically, however. As discussed elsewhere,⁷⁻⁹ pseudopotential techniques now make it possible to ex-

cute *ab initio* calculations with accuracies approaching and in some instances exceeding the Hartree-Fock level on molecules as heavy as XeF₆ and IF₇. Therefore, it seemed appropriate to investigate whether the newly available quantum tools offer useful characterizations of such substances.

Our initial attack in this sparsely mapped out area is to determine how well the pseudopotential approach performs when applied, in conjunction with various basis sets, to the simpler polyatomic compounds. An assessment of the performance prior to studies of unknown properties can be based on the degree to which calculations can reproduce structures and force constants generated by experiment or all-electron *ab initio* theory. It must be emphasized that the approach herein described is genuinely *ab initio*, involving no freely adjustable parameters to help fit observables. It is, however, quite as dependent upon the choice of basis set as are other *ab initio* methods. In addition, it is fair to mention that the formulation of practical effective potentials is not altogether free of arbitrariness; some aspects of the influence of the choice upon the derived force field have been discussed elsewhere.^{7,8}

In this paper we shall establish preliminary basis sets and investigate the structures and force fields of XeF₂ and XeF₄. Nonbonded interactions, which might be expected to become increasingly significant in more crowded molecules such as XeF₆ and IF₇, are estimated roughly by using F₂···F₂ as a model system. We also develop for use in subsequent papers a formalism to aid in the interpretation of steric effects upon potential energy surfaces.

II. PROCEDURE

A. Pseudopotential method

The computational method adopted in the present research is described in detail in Ref. 8. It is a valence-

only LCAO-MO procedure incorporating the molecular Phillips-Kleinman pseudopotential operator

$$V^{PP} = \sum_i^{\text{valence}} \sum_j^{\text{core}} \sum_k^{\text{nucl}} |\phi_{ck}^j\rangle \times (\epsilon_v^i - \epsilon_{ck}^j) \langle \phi_{ck}^j | \left(1 - \sum_{I \neq i}^{\text{valence}} |\chi_v^I\rangle \langle \chi_v^I| \right) \quad (2.1)$$

in the molecular Fock equations

$$(F + V^{PP}) \chi_v^i = \epsilon_v \chi_v^i \quad (2.2)$$

to prevent the collapse of the molecular valence pseudo-wave functions χ_v into the region of the core atomic orbitals ϕ_c when the latter are retained in their free-atom form with no explicit constraints for orthogonality to the valence orbitals. In addition, the full Fock operator F in Eq. (2.2) is replaced by the operator-equivalent quantity $(\hat{F} + W^i)$, where \hat{F} is the Fock operator for valence electrons only, and W^i is a contribution to the effective potential derived as outlined in Ref. 8. The method is *ab initio* in its entirety, as neither the V^{PP} nor W^i contain adjustable parameters. Our calculations differ from those described previously⁸ in (a) the adoption of a seven-term instead of five-term Gaussian representation of W^i and (b) in the use of individual W^i functions instead of an average \bar{W} , for s and p orbitals. Parameters for these Gaussian representations are listed in Table I.

B. Basis sets

Two basis sets, the second of which is listed in Table II, were developed. Basis set I (BAS I) consists of minimal sets of fluorine and xenon functions from atom-optimized sets of STO's.¹⁰ Each basis function in BAS I is an STO-4G representation with Gaussian coefficients and exponents assigned by Stewart's expansion procedure.¹¹

TABLE I. Coefficients and exponents for the Gaussian expansion of the local potentials (W^i) corresponding to basis set II. The form of the expansion is defined by Eq. (23), Ref. 8.

Fluorine			
2s coefficient	2s exponent	2p coefficient	2p exponent
0.560884	77.2279	0.262094	176.954
0.814871	34.7262	0.293606	55.0692
-0.093754	24.2844	0.165350	26.5443
0.289322	12.0663	0.101523	12.2773
0.010077	3.48607	0.005176	10.3241
0.003545	1.92849	0.013960	1.50365
0.003970	1.03452	0.004355	0.206203
Xenon			
5s coefficient	5s exponent	5p coefficient	5p exponent
0.452298	39.5841	-0.137622	10.3342
-0.089524	7.55159	0.304014	3.27004
0.238609	3.48139	0.138402	1.68770
0.156826	2.00564	-0.032131	1.39014
0.007677	0.940737	0.014245	0.659924
0.011372	0.615187	0.002858	0.160287
0.001370	0.078437	0.000217	0.000181

TABLE II. Contraction coefficients and Gaussian exponents (in a.u.) for basis set II.

Orbital	Coefficient	Exponent
F 1s	0.0174758	1126.16
	0.122523	169.743
	0.434999	38.1815
	0.559812	10.2120
F 2s	0.053879	21.4954
	0.081660	4.98978
	-0.554826	1.40357
	-0.567619	0.422048
F 2p	0.046778	21.4954
	0.229667	4.98978
	0.479553	1.40357
	0.480520	0.388069
Xe 5s	-0.520877	1.200118
	0.267082	0.679404
	0.602430	0.316361
	0.510153	0.138100
Xe 5p	-0.0923311	1.973054
	0.491836	0.415885
	0.443485	0.170986
	0.188419	0.089137

After it became apparent that BAS I yields molecular information of mediocre quality, we undertook the construction of an improved basis set, paying special attention to the achievement of a better valence shell distribution than is afforded by a minimal STO set.

This basis set (BAS II), also minimal, was generated to take greater advantage of the flexibility inherent in contracted functions of four Gaussians than is obtained by forcing them to simulate single-zeta STO's. In the case of fluorine we carried out an SCF calculation, via Gaussian 70,¹² at the 4-31G level. This unrestricted Hartree-Fock program (one electron for each orbital), applied to the open-shell fluorine atom, generates separate orbitals for α and β spins. Compromise averages of the α and β AO's so derived were computed subjectively; these were then fed into an alternative atomic restricted SCF calculation¹³ to improve the smallest exponents of the 2s and 2p Gaussians. The resultant four-Gaussian basis functions were adopted for BAS II.

In the case of xenon, BAS II retained the contracted functions of BAS I for the core orbitals 1s through 4d. Valence 5s and 5p orbitals, however, were constructed from Clementi's double zeta STO treatment of xenon,¹⁰ as follows: From the 5s and 5p orbitals of Clementi, composed of (1s, 1s', 2s, ..., 5s, 5s') and (2p, 2p', ..., 5p, 5p') linear combinations, were lifted the coefficients and exponents of the 5s, 5s' and 5p, 5p' primitives. Contracted four-Gaussian representations of these double-zeta components were then determined with the aid of the program GAUSFIT,¹⁴ and incorporated into BAS II.

C. Characterizations of potential surface

For the lower xenon fluorides XeF_2 and XeF_4 , expansions of the potential energy

$$V(S_i) = \sum_i f_i \tilde{S}_i + (1/2) \sum_i \sum_j f_{ij} \tilde{S}_i \tilde{S}_j + (1/6) \sum_i \sum_j \sum_k \tilde{f}_{ijk} \tilde{S}_i \tilde{S}_j \tilde{S}_k \quad (2.3)$$

were carried out in terms of curvilinear stretch and bend symmetry coordinates \tilde{S}_i reckoned, for sake of comparison, both from the experimental mean and the theoretical equilibrium structures. Schwendeman¹⁵ has cited evidence favoring the evaluation of force constants by expanding about the experimental rather than theoretical equilibrium structure. If there is a difference between experimental and theoretical structures, of course linear terms f_i of Eq. (2.3) necessarily enter as evidence of the deficiencies in the theoretical computations. In the present work cubic constants were derived only for the totally symmetric modes and expressed in terms of the Morse parameter a computed as if each of the n bonds stretched as an independent Morse oscillator, by the relation

$$a = -\sqrt{n} \tilde{f}_{111} / 3f_{11}. \quad (2.4)$$

Although force fields are most efficiently derived from *ab initio* computations by the force method made practical by Pulay,¹⁶ the present work found the Taylor series coefficients of Eq. (2.3) from direct calculations of molecular energies as a function of symmetry coordinates. Definitions of symmetry coordinates consistent with those used in the following are given, for XeF₄, by Yeranos¹⁷ and, for XeF₆, by Bartell and Gavin.³

In our calculations of frequencies based on an experimental reference structure, we use the quadratic terms of Eq. (2.3), discarding the remainder as spurious. Calculations of frequencies followed the Wilson FG matrix method¹⁸ or were carried out by Hilderbrandt's approach.¹⁹

D. Role of nonbonded interactions

A large body of literature²⁰ attests to the substantial role of nonbonded repulsions in molecular force fields, particularly when smaller central atoms than xenon are involved. When it became apparent that results with BAS I, based on STO's, underestimated the cost of deformations in which F atoms are compressed together, it was natural to enquire into the nonbonded contribution. Single-zeta STO minimal basis sets are known to yield fluorine atoms that are much too small. In order to get a qualitative or semiquantitative inference of magnitudes we estimated F...F nonbonded interactions

$$V(q) - V(q_0) = V'(q_0) \Delta q + \frac{1}{2} V''(q_0) (\Delta q)^2 + \dots \equiv F' q_0 \Delta q + \frac{1}{2} F (\Delta q)^2 + \dots, \quad (2.5)$$

where F' and F are the conventional Urey-Bradley force constants and $\Delta q = (q - q_0)$, with q_0 any desired reference distance, by computing F₂...F₂ interaction energies as a function of F...F distances q for D_{2d} geometries, by the procedure of Sec. II.A. Now, force constants for the xenon fluorides can be expressed in terms of the Urey-Bradley constants, and these, in turn, can be estimated from F₂...F₂ interactions for any basis set desired. Therefore, it is possible to diagnose

the degree to which the variations in potential surface from basis set to basis set can be ascribed to variations in "classical nonbonded interactions." Whatever variation is left over then is attributable to "bond interactions."

It is in the bending force constants that the most prominent nonbonded contributions are expected. As is customary in Urey-Bradley (UB) treatments, only the geminal and not the more remote *trans* nonbonded interactions will be considered. Therefore, nonbonded considerations are of concern for XeF₆ and in-plane bends of XeF₄ but not for XeF₂. For XeF₄ the relevant UB quadratic bending force constants are, for both the b_{1g} and e_u deformations,¹⁷

$$f = H - \frac{1}{2} F' + \frac{1}{2} F, \quad (2.6)$$

where H is the UB force constant for a geminal F-Xe-F bend, and where the unimportant constant H' is here disregarded.

For XeF₆, to be treated in the following paper, it is the t_{1u} constants for deformation from O_h symmetry that are of primary concern because the molecule spontaneously deforms along the t_{1u} direction. The quadratic constant is

$$f(t_{1u}) = H - \frac{3}{2} F' + \frac{1}{2} F, \quad (2.7)$$

where the full contribution of F' introduced by the redundancy relation is retained.²¹ Some authors balance off 2/3 of the F' contribution²² against an H' contribution but there is no physical reason for doing so.

Inasmuch as the degree of deformation attained along a t_{1u} coordinate before forces are balanced (at the equilibrium structure) depends crucially upon the quartic as well as the (negative) quadratic constant, it is of especial interest to assess the nonbonded contribution to the quartic constants. For simplicity, we examine the quartic constants \tilde{f}_{4444} and $\tilde{f}_{444'4'}$ of Vernon,²³ the only published force constants based on a central forces model. Vernon's constants were expressed in terms of a points-on-a-sphere model potential employing pairwise additive contributions, analogous to those of Eq. (2.5), having the form

$$V(q) = Kq^{-n}, \quad (2.8)$$

where K and n can be adjusted to fit the F...F potential curve in the range of interest. When considering only geminal interactions, Vernon's constants become

$$\tilde{f}_{4444} = \frac{2^{-n/2}}{96} \left[\frac{n(n+4)}{4} + \frac{n(n+2)}{64} (n^2 + 10n + 48) \right] \quad (2.9)$$

and

$$\tilde{f}_{444'4'} = \frac{2^{-n/2}}{96} \left[n - \frac{5n(n+2)}{4} + \frac{3n(n+2)(n+4)}{8} + \frac{n(n+2)(n+4)(n+6)}{64} \right], \quad (2.10)$$

in units of $(2Kr^{-n})$, where r is the sphere radius, in the appropriate limit with his parameter β taken as zero.

TABLE III. Results for atomic fluorine. Orbital energies and total energies are in hartree.

	RHF limit ^a	SCF ^b	STO-SZ ^c	STO-DZ ^d	BAS I	BAS II
1s	-26.383		-26.303	-26.374	-26.185	-26.233
2s	-1.5726		-1.4306	-1.5670	-1.4231	-1.5333
2p	-0.7300		-0.5261	-0.7244	-0.5214	-0.6843
E_T	-99.4093	-99.2655	-98.9421	-99.4012	-98.6566	-99.2361

^aReference 24.^cAtom-optimized single-zeta exponents from Ref. 10.^bGaussian 70.^dAtom-optimized double-zeta exponents from Ref. 25.

TABLE IV. Results for atomic xenon. Orbital energies and total energies are in hartree.

	RHF limit ^a	STO-SZ ^b	STO-DZ ^c	BAS I	BAS II	SZ core, ^b DZ valence ^c
1s	-1224.4	-1224.29	-1224.39	-1219.98	-1219.90	-1224.45
5s	-0.9444	-0.8045	-0.9420	-0.8020	-0.8590	-0.8938
5p	-0.4573	-0.3592	-0.4551	-0.3584	-0.4238	-0.4507
E_T	-7232.15	-7219.79	-7232.12	-7207.14	-7207.35	-7220.11

^aReference 24.^bSingle-zeta atom optimized exponents from Ref. 10.^cDouble-zeta atom-optimized exponents from Ref. 25.

III. RESULTS

A. Atomic calculations

In Tables III and IV are listed total energies and orbital energies for selected orbitals of fluorine and xenon. Full atomic SCF calculations based on BAS I and BAS II are presented and compared with results of other studies. Set BAS I is seen to give results similar to those of the single-zeta STO calculation it was modeled after. A very significant improvement is seen in BAS II although, limited by its minimal basis, it does not fully attain the accuracy obtained with the more flexible bases it is compared with. Another clear manifestation of the advantage of BAS II over BAS I is seen in the next section.

B. Nonbonded interactions

Fluorine-fluorine nonbonded interactions were inferred by subtracting from the energy of the $D_{2d}F_2 \cdots F_2$ system the energy of two isolated F_2 molecules. Bonded internuclear distances were frozen at 1.417 Å in all calculations, a constraint found elsewhere²⁶ to give results insignificantly different from those obtained when the bonded distance is allowed to relax. Tabulated in Table V are interaction energies as a function of nonbonded distance, for BAS I and BAS II as calculated by the pseudopotential method of Sec. II.A. Included for comparison are results of all-electron calculations corresponding to STO-3G and 4-31G of Gaussian 70. Results for BAS I and STO-3G are closely similar as might be expected from their minimal basis, single-zeta STO origins. These results, however, imply interaction energies only about 1/3 of those given by BAS II and 4-31G, consistent with the fact that minimal STO bases make second-row atoms too small. Even though BAS II has only half as many variational parameters in its valence shell as does 4-31G, it gives results that are comparable and, indeed, slightly closer to the modestly

larger estimates of $F \cdots F$ interactions obtained by another method.²⁷

Analytical representations of the BAS I and BAS II results derived from the outer points in Table V, for computations of Urey-Bradley parameters are, in mdyn Å,

$$V(q) \approx 14\,230 e^{-6.24q}, \quad (3.1a)$$

$$\approx 6\,500 q^{-16.17} \quad (3.1b)$$

for BAS I and

$$V(q) \approx 908 e^{-4.71q}, \quad (3.2a)$$

$$\approx 500 q^{-12.2} \quad (3.2b)$$

for BAS II. Exponential representations (3.1a) and (3.2a) follow $V(q)$ somewhat more faithfully but the alternative expressions are needed for Eqs. (2.9) and (2.10).

C. Xenon fluorides

Orbital energies for XeF_2 and XeF_4 , as computed by the procedure of Sec. II.A, are compared in Tables VI and VII with those derived from the all-electron calculation of Basch, Moskowitz, Hollister, and Hankin,²⁴ who used a larger basis set, consisting of a double-zeta valence basis and single-zeta core. Also compared, for sake of illustration, are ionization potentials observed by ESCA and calculated by the $X\alpha$ method.

TABLE V. Fluorine-fluorine nonbonded interaction energies $0.25 \times [E(F_2 \cdots F_2) - 2E(F_2)]$ in hartree.

F...F distance (Å)	STO-3G ^a	4-31G ^a	BAS I ^b	BAS II ^b
2.2070	3.395×10^{-3}	6.595×10^{-3}	3.412×10^{-3}	6.510×10^{-3}
2.5005	4.760×10^{-4}	1.379×10^{-3}	5.475×10^{-4}	1.602×10^{-3}
2.6854	1.294×10^{-4}	3.905×10^{-4}	1.723×10^{-4}	6.695×10^{-4}

^aAll-electron calculation, Gaussian 70.^bValence electrons only, pseudopotential results.

TABLE VI. Orbital energies and ionization energies of XeF₂ as determined by various calculations and by experiment. Energies are in hartree.

Orbital	Orbital energies			Ionization energies		
	SCF ^a <i>r</i> = 2.000 Å	BAS II 2.000 Å	BAS II ^b 2.064 Å	ESCA ^c exptl.	X α (rel.) ^d 2.000 Å	X α (nonrel.) ^d 2.000 Å
8 σ_g	-1.4863	-1.4168	-1.4093	1.331
5 σ_u	-1.4821	-1.4127	-1.4062	1.331
9 σ_g	-1.0083	-1.0103	-1.0111	0.9658	0.853	0.805
6 σ_u	-0.6753	-0.6317	-0.6206	0.6391	0.636	0.636
4 $\pi_{u1/2}$	-0.6359	-0.6008	-0.5936	0.5832	0.566	0.566
4 $\pi_{u3/2}$	-0.6359	-0.6008	-0.5936	0.5832	0.562	0.566
3 π_g	-0.5871	-0.5169	-0.5161	0.5266	0.555	0.555
5 $\pi_{u1/2}$	-0.4994	-0.4662	-0.4740	0.4649	0.423	0.401
5 $\pi_{u3/2}$	-0.4994	-0.4662	-0.4740	0.4649	0.393	0.401
10 σ_g	-0.4696	-0.3504	-0.3481	0.5006	0.526	0.518
7 σ_u	+0.0498	+0.0859	+0.0522		0.239	0.246
E_{VT} ^e		-62.7691	-62.7729			

^aReference 24.^bPresent work at theoretical bond length of minimum energy.^cReference 28.^dReference 29.^e E_{VT} is sum of the valence electronic energy E_{VEE} and the valence nuclear repulsion energy E_{VNR} , where E_{VNR} is the sum of the nuclear-nuclear repulsion energies calculated by taking charges to be $(Z - N_{core})$. E_{VEE} is the electronic energy corresponding to valence molecular orbitals.

Prior *ab initio* calculations of the bond lengths and σ_g force constant of XeF₂ have been reported.³⁰ No comparable results are available for the σ_u or π_u force constants, however, or of the structure and force field of XeF₄. In Tables VIII-X are presented our pseudopotential computations of bond lengths, force constants, and frequencies for XeF₂ and XeF₄, together with published results for the same quantities.^{17,31-36}

For supplementary material on atomic and molecular wave functions for the xenon fluorides, see Ref. 32 of the following paper.³⁷

IV. DISCUSSION

As is documented in Tables VI and VII, the present pseudopotential SCF calculations with BAS II yield

TABLE VII. Orbital energies^a and ionization energies of XeF₄ as determined by various calculations and by experiment. Energies are in hartree.

Orbital	Orbital energies			Ionization energies	
	SCF ^b <i>r</i> = 1.950 Å	BAS II 1.958 Å	BAS II 2.037 Å	BAS I 1.958 Å	ESCA ^c exptl.
8a _{1g}	-1.6024	-1.5128	-1.4932	-1.4480	1.374
5e _u	-1.5680	-1.4895	-1.4768	-1.4203	
4b _{1g}	-1.5417	-1.4781	-1.4690	-1.4035	1.021
9a _{1g}	-1.0440	-1.1226	-1.1238	-0.9986	
6e _u	-0.7820	-0.7437	-0.7260	-0.6254	0.6645
4a _{2u}	-0.7586	-0.7240	-0.7076	-0.6169	0.7255
3b _{2g}	-0.6729	-0.5905	-0.5840	-0.4167	0.5715
3e _g	-0.6619	-0.5808	-0.5775	-0.4164	
1b _{2u}	-0.6579	-0.5767	-0.5747	-0.4151	0.4858
7e _u	-0.6450	-0.5600	-0.5597	-0.3998	
1a _{2g}	-0.6314	-0.5545	-0.5579	-0.4024	0.4858
5b _{1g}	-0.6074	-0.4756	-0.4552	-0.2761	
5a _{2u}	-0.5547	-0.5107	-0.5224	-0.3621	0.4858
10a _{1g}	-0.4649	-0.3516	-0.3580	-0.1547	
8e _u	0.0002	0.0275	-0.0154	0.2008	
E_{VT} ^d		-110.4490	-110.4598	-108.5376	

^aConvention for designating irreducible representations (atoms on axes) follows literature on orbital energies but is inconsistent with convention of Tables IX and X.^bReference 24.^cReference 28.^dSee footnote e, Table VI.

TABLE VIII. Frequencies (cm^{-1}) and force constants ($\text{mdyn}/\text{\AA}$) of XeF_2 .

Type	BAS II ^a	BAS II ^b	CI ^c	Experiment
$\nu_1(\sigma_g)$	549	631	483	514.5 ^d
$\nu_2(\pi_u)$	222	245		215 ^e
$\nu_3(\sigma_u)$	583	685		549 ^e
$F_{11}(\sigma_g)$	3.37	4.45	2.607	2.962 ^f
$F_{22}(\pi_u)$	0.214	0.260		0.201 ^f
$F_{33}(\sigma_u)$	2.95	4.08		2.62 ^f

^aCalculations correspond to bond length of 2.068 \AA at the pseudopotential SCF minimum energy.

^bCalculations correspond to bond length of 2.00 \AA originally reported as the experimental internuclear distance in Ref. 31. Calculations at 1.977 \AA , the more recent result, would increase stretching force constants by about 11% and frequencies by about 5%.

^cDetermined from Ref. 30, a "double-zeta plus polarization" quality configuration interaction calculation. The energy minimum corresponds to a bond length of 1.999 \AA .

^dReference 33.

^eReference 34.

^fCalculated from experimental frequencies.

valence orbital energies agreeing in order with those of the more flexible, all-electron SCF calculations of Basch *et al.*,²⁴ in every case but one, the b_{1g} , a_{2u} pair of XeF_4 . It is also evident how much superior the minimum set BAS II is in comparison with the STO set BAS I. The SCF ordering is similar to that of the experimental ESCA ionization potentials²⁸ although there is no compelling reason for the two disparate quantities to agree precisely. Model $X\alpha$ calculations²⁹ of electronic binding energies in XeF_2 based on an approximate "transition state" procedure, on the other hand, are in closer agreement with the ESCA results.

For each molecule the present calculations lead to the correct geometric configuration. Although this is unremarkable in the case of $\text{XeF}_2(D_{\infty h})$ for which Walsh's rules³⁹ apply in a straightforward way, it is of some interest for $\text{XeF}_4(D_{4h})$. Empirical molecular orbital calculations⁴⁰ make XeF_4 deform spontaneously along an e_u coordinate, via the agency of an in-plane lone pair protruding between two ligands, if the 5s orbital is insufficiently lower in energy than the 5p orbitals (more about which will be given later). Also, Gillespie's simple "valence-shell-electron-pair-repulsion" (VSEPR) model^{41,42} has been applied to XeF_4 . This is of special interest because Gillespie was alone among theorists in forecasting correctly the structure of XeF_6 .⁴² Now, the VSEPR approach treats XeF_4 as an "AX₄Y₂" case in which the Y groups can be taken to represent either lone pairs, or bond pairs to atoms that are not as electronegative as the X atoms. This choice is not supposed to make a difference in the structural outcome. In practice, however, it turns out that true hexacoordinate molecules AX₄Y₂ tend not to be D_{4h} but, rather C_{2v} , with Y groups *cis* to each other.⁴³

Bond lengths yielded by the present treatment (2.068 \AA for XeF_2 and 2.037 \AA for XeF_4), while too long, are less than 5% in error for BAS II. The contraction of 0.03 \AA observed experimentally^{31,32} upon going from XeF_2

to XeF_4 is correctly reproduced by the calculations.

Stretching force constants evaluated about the experimental reference lengths are appreciably high. That the error decreases substantially when the theoretical minimum is used is to be regarded as a fortuitous cancellation of two errors brought about by anharmonicity, i. e., as internuclear distances increase, V'' falls. The rate of fall corresponds to a Morse parameter a defined in Eq. (2.4) of 1.58 \AA^{-1} for XeF_2 (at 1.977 \AA) and 1.61 \AA^{-1} for XeF_4 (at 1.95 \AA). According to the empirical derivative functions of Herschbach and Laurie,⁴⁴ Xe-F single bonds might be expected to exhibit Morse parameters of 1.80 and 1.85 \AA^{-1} at distances of 1.977 and 1.95 \AA , respectively. Therefore, the Morse anharmonicity implied by the present calculation is close to the expected magnitude.

Bending force constants and frequencies evaluated at the experimental bond lengths are in appreciably better agreement with experiment than are the corresponding stretching quantities. One calculated bending frequency, the e_u frequency for XeF_4 , is conspicuously low. It is not as low for BAS II as for the poorer basis set BAS I, however. Since the STO's in BAS I lead to nonbonded interactions that are markedly too weak [see Eqs. (3.1) and (3.2)] and hence to in-plane bending constants that are too small [see Eq. (2.6)], it is worthwhile to see how much of the deficiency of BAS I can be attributed to steric factors. According to Eqs. (2.6), (3.1), and (3.2) by virtue of the differences in constants F and F' , the in-plane bend constants for BAS II should be 0.015 $\text{mdyn}/\text{\AA}$ greater than for BAS I. In fact, the *total* increases were found to be 0.044 $\text{mdyn}/\text{\AA}$ for b_{1g} and 0.087 $\text{mdyn}/\text{\AA}$ for e_u , showing that deficiencies of STO's in Xe-F in *bonding* interactions are even more severe than in F...F *steric* interactions. Indeed, the low 0.016 $\text{mdyn}/\text{\AA}$ e_u bending force constant obtained with BAS I shows that this basis implies an XeF_4 molecule perilously close to undergoing a spontaneous second-order Jahn-Teller deformation along an e_u bending coordinate. Even

TABLE IX. Frequencies (cm^{-1}) of XeF_4 .

Vibration ^a	BAS II ^b	BAS I ^c	Experiment
$\nu_1(a_{1g})$	579	692	554.3 ^d
$\nu_5(b_{2g})$	521	655	524 ^d
$\nu_6(e_u)$	601	731	586 ^e
$\nu_2(a_{2u})$	281	319	291 ^e
$\nu_3(b_{1g})$	186	218	218 ^d
$\nu_4(b_{1u})$	171	189	216 ^{d,f}
$\nu_7(e_u)$	111	128	161 ^{d,f}

^aConvention for designating irreducible representations (atoms between axes) follows literature on vibrations but is inconsistent with convention of Table VII.

^bCalculations correspond to bond length 2.037 \AA at the pseudopotential SCF minimum energy.

^cCalculations correspond to bond length 1.958 \AA . Experimental internuclear distance is 1.95 \pm 0.01 \AA (Ref. 35).

^dReference 33.

^eReference 36(a).

^fCalculated from overtones.

TABLE X. Force constants (mdyn/Å) for XeF₄.

Type ^b	Theoretical		Experiment ^a			
	BAS II ^c	BAS II ^d	A ^e	B ^f	C ^g	D ^h
$F_{11}(a_{1g})$	3.75	5.37	3.439	3.3039	3.30	3.45
$F_{55}(b_{2g})$	3.04	4.73	3.07	2.8238	2.82	3.03
$F_{66}(e_u)$	2.94	4.37		2.6534	3.06	3.24
$F_{22}(a_{2u})$	0.280	0.361	0.300	0.3004	0.300	0.290
$F_{33}(b_{1g})$	0.096	0.133	0.133	0.1547	0.154	0.134
$F_{44}(b_{1u})$	0.164	0.200	0.261	0.2736	0.300	0.268
$F_{77}(e_u)$	0.079	0.103		0.1226 ^f	0.154	0.134
$F_{67}(e_u)$	-0.235	-0.318		-0.3448	-0.139	

^aSee the text and Ref. 38.

^bSee footnote a, Table IX.

^cCalculations correspond to bond length of 2.037 Å at the SCF pseudopotential minimum energy.

^dCalculations correspond to bond length of 1.958 Å. Experimental internuclear distance is 1.95 ± 0.01 Å (Ref. 35).

^eCalculated from observed frequencies in Table IX.

^fReference 36(b).

^gReference 17.

^hCalculated from hybrid orbital force field of Ref. 33.

ⁱNumerical value too low; it is based on an early, incorrect assignment of $\nu_7 = 123 \text{ cm}^{-1}$ instead of the revised assignment of $\nu_7 = 161 \text{ cm}^{-1}$ (Ref. 33).

BAS II yields a stereochemical activity of the in-plane lone pair that is excessive (i.e., an e_u force constant that is somewhat too small). Whether this is a deficiency of the basis set, an inadequacy of a single configuration wave function, or a hint that a relativistic increase in the 5s-5p energy split is needed to make the lone pair less "active," is not yet known.

One further aspect of F-Xe-F bonding as inferred from force constants deserves comment. If displacements are transformed from symmetry coordinates to internal coordinates, the associated stretch-stretch interaction force constants for XeF₂ are 0.18, 0.21, and 0.17 mdyn/Å for calculated (experimental r), calculated (theoretical r), and experiment,⁴⁵ respectively. The analogous theoretical *trans* interaction constants for XeF₄ are 0.36 and 0.23 mdyn/Å. Corresponding theoretical *cis* interaction force constants for XeF₄ are somewhat smaller, at 0.14 and 0.18 mdyn/Å. Unfortunately, reliable experimental interaction constants for XeF₄ are not available for comparison.³⁸ In sign, then, and in magnitude the calculated constants are consistent with experiment. Both are in accord with important contributions from the Pauling ionic resonance structures F-Xe⁺...F⁻, etc., supposed to provide a rationale for hypervalent bonding in the framework of the octet theory without invoking valence d orbitals.^{46,47} In the present calculations, it is to be recalled, d orbitals were not included in the basis set, yet fairly good results for the molecules were obtained. A much more extensive theoretical investigation by Bagus *et al.*³⁰ confirms that single configuration MO calculations for XeF₂ yield reasonable bond lengths and σ_r force constants (other force constants were not calculated), that the bonding is, in fact, well represented by the ionic resonance structures, and that d orbitals are of only quantitative, not qualitative, importance.

On the other hand, SCF wave functions are, of course, quite incapable of yielding dissociation energies. Not even multiconfiguration wave functions were found to yield dissociation curves of reasonable shape for XeF₂ unless a considerable number of configurations was included.³⁰

Properties of krypton difluoride exhibit a striking contrast to those of the xenon homolog.^{47,48} Stretch-stretch interaction constants of opposite sign and significantly different electronic behavior—related to the fact that KrF₂ is marginally bonded—are discussed clearly by Coulson⁴⁷ and by Bagus *et al.*⁴⁹

From the foregoing it can be seen that the present pseudopotential approach with a minimum basis set gives a reasonably faithful account of the structure and force field of two of the lower fluorides of xenon. It is clear that d orbitals on xenon, excluded from the present calculations, are hardly the *sine qua non* of hypervalent bonding. Results, indeed, are sufficiently promising to offer hope that a similar analysis of the imperfectly understood molecule XeF₆ would be enlightening. Such an analysis will be presented in the following paper.

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