Pseudopotential SCF–MO studies of hypervalent compounds. II. XeF$_5^+$ and XeF$_6$

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New evidence bearing upon the anomalous properties of xenon hexafluoride has been obtained via the *ab initio* molecular orbital approach applied successfully to the di- and tetrafluorides in paper I. Structures of both XeF$_5^+$ and XeF$_6$ are governed by a stereochemically active lone pair. In the case of the square–pyramidal cation the F$_{ax}$–Xe–F$_{eq}$ angle calculated for the bare ion is within 2° of the value observed in the crystalline complex. For the hexafluoride, however, the calculated deformation from O$_h$ symmetry is appreciably greater than that deduced from electron diffraction intensities. Nevertheless, the results of calculations are in sufficient conformity with the Bartell–Gavin, Pitzer–Bernstein interpretation and at variance with the "electronic-isomers" interpretation to leave little doubt about the answer. With increasing fluorination in the XeF$_n$ series the HOMO–LUMO energy difference decreases and the second-order Jahn–Teller effect is enhanced. Increasing fluorination (and increased positive charge on Xe) also shortens bond lengths; calculated shortenings parallel observed shortenings. The deformation of XeF$_6$ from O$_h$ is along t_{1u} bend and stretch coordinates to a C$_{3v}$ structure with long bonds adjacent to the lone pair, as expected according to the valence-shell–electron-pair-repulsion model. Pure t_{2g} deformations are destabilizing but anharmonic t_{1u}–t_{2g} coupling significantly stabilizes the deformation. Steric aspects of the structure and force field are diagnosed and found to be minor. Values for the force constants f_{44}, f_{55}, $\bar{f}_{4444}$, $\bar{f}_{444'4'}$, and $\bar{f}_{445}$ are derived and found to be of the magnitude forecast in the Bartell–Gavin and Pitzer–Bernstein treatments except that the calculations do not reproduce the delicate balances believed to lead to almost free pseudorotation in XeF$_6$.

I. INTRODUCTION

Of the rare-gas compounds synthesized to date, xenon hexafluoride has exhibited the most puzzling behavior. Different physical properties have been interpreted in terms of quite different electronic or structural representations, and no interpretation has been universally accepted.[1-8] Electron diffraction studies[5,9,10] provided the earliest clues for the molecular description now most commonly advanced. According to this description, first proposed by Bartell and Gavin,[5] the molecule is distorted just far enough from a regular octahedron to be able to execute a large amplitude pseudorotation in the subspace of the t_{1u} displacements; it is not distorted so far that it is frozen into a static deformation. By implication, the molecule is polar at any arbitrary point along its pseudorotational pathway, but its dipole moment averages to zero in any given vibrational state. In an alternative interpretation, Goodman[8] proposed that XeF$_6$ exists in thermally excited "electronic isomers" suffering first-order Jahn–Teller distortions. A variety of thermodynamic,[4] spectroscopic,[11-13] and magnetic and electric-field deflection,[6,7,14,15] as well as more elaborate electron diffraction experiments,[16] have added valuable evidence.

Several years ago Pitzer and Bernstein[17] reviewed the available information and synthesized a semiquantitative model, based on the pseudorotation description, that was consistent with all prior evidence except for certain time-dependent observations[11] deemed to be spurious.[18] While the Pitzer–Bernstein treatment has considerable merit, it fails to persuade some experimentalists who express concern that concrete evidence for the polar deformation and pseudorotation is still lacking.

Because the enigmatic, exceedingly reactive molecule has proven to be troublesome for experimentalists, it presents a challenging target for theorists. Although Gillespie, with his qualitative valence-shell-electron-pair-repulsion (VSEPR) theory,[19] correctly forecast some of the principal structural features of XeF$_6$, quantum theorists employing semiempirical molecular orbital methods initially found no evidence of deformations from a regular octahedron.[20] After experimental evidence of deformations was found,[3] other molecular orbital studies of comparable quality were carried out that supported the new experimental inferences.[5,21]

Rigorous, *ab initio* molecular orbital calculations to resolve the problem were quite out of the question for years. Therefore, several alternative semiempirical techniques were applied. Among these, the crystal-field model of Wang and Lohr[22] and Xα molecular orbital calculations[23] added useful perspectives.

One remarkable all-electron SCF–MO calculation upon xenon hexafluoride by Basch *et al.*[24] was carried out, imposing O$_h$ symmetry. Based on single zeta core and double zeta valence orbitals, its primary purpose was to compare electronic trends in the series XeF$_2$, XeF$_4$, and XeF$_6$. Unfortunately, such treatments are, even today, too demanding computationally to offer a practical means of mapping out the potential surface of such a heavy molecule as the hexafluoride.

For the above reasons it is of especial interest to apply the *ab initio* pseudopotential approach described in paper I[25] to the case of xenon hexafluoride. Because the method is considerably more economical than alternative *ab initio* methods, yet competitive in accuracy in
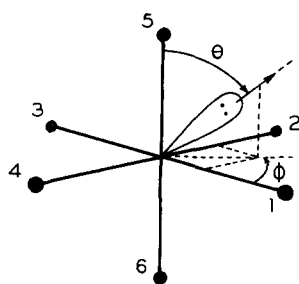
FIG. 1. Numbering scheme for XeF_6 used in Eqs. (2.3)–(2.5). Angles θ and ϕ for the t_{1u} coordinates of Eqs. (2.7) and (2.8) correspond to the directions of the lone pair.

the calculation of force fields, we undertook such a study and describe it in the following.

Although the first two xenon compounds investigated, XeF_2 and XeF_4, gave very promising results,[25] as did iodine fluoride,[26] none of these examples provided a good illustration of the "degree of stereochemical activity" of a heavy atom lone pair. Inasmuch as such a consideration might be crucial in the case of XeF_6, we decided to examine the somewhat simpler example, XeF_5^+ as well, where the known distortion[27,28] of its F_{ax}–Xe–F_{eq} angles from 90° offers a useful gauge of the influence of the xenon lone pair.

II. BACKGROUND MATERIAL

Computational procedures employed in this research are discussed in paper I,[25] where the pseudopotential method, the development of basis sets, and aspects of potential surfaces are presented. In this section we discuss the displacement coordinates of XeF_5^+ and XeF_6, and the procedures used to examine the potential surface.

For XeF_5^+ only the a_1 symmetry coordinates S_1 (axial stretch, ΔR), S_2 [equatorial in-phase stretch $(\Delta x_1 + \Delta x_2 + \Delta x_3 + \Delta x_4)/2$], and S_3 (out-of-plane bend) are of interest in the determination of the equilibrium structure. The linear combinations

$$S_a = 5^{-1/2}(S_1 - 2S_2) \tag{2.1}$$

and

$$S_b = 5^{-1/2}(2S_1 + S_2) \tag{2.2}$$

are particularly convenient adjunct coordinates. The method we applied to find the SCF structure reported below was as follows: First, with r_{eq} and r_{ax} fixed at the values 1.84 and 1.79 Å, respectively, observed[28] in the crystalline complex with RuF_6^-, we found the angle F_{eq}–Xe–F_{ax} which minimized the calculated energy. Then, retaining this angle and keeping S_a constant [thereby fixing $(r_{eq} - r_{ax})$], we minimized the energy with respect to displacement S_b. Since these moves gave a result close to the potential minimum, it was now possible to establish, with the computation of three more points, the parameters characterizing the paraboloid $V(S_a, S_b)$. Fixing S_a and S_b at the values minimizing $V(S_a, S_b)$, we again varied S_3. The structure corresponding to the minimum energy in this operation was accepted as our final structure.

Figures illustrating the symmetry coordinates of xenon hexafluoride are published in Refs. 5 and 17. In

keeping with the symmetry of the Hamiltonian and for convenience, we express the intramolecular displacements relative to an O_h reference structure instead of one of the (eight equivalent) equilibrium C_{3v} structures believed to correspond to potential minima. This means that the t_{1u} bending quadratic force constant is expected to be *negative* as a consequence of a spontaneous t_{1u} second-order Jahn–Teller deformation[5] from O_h symmetry—a deformation interpretable in terms of the stereochemical activity of the lone pair on xenon. It means, also, that it is essential to retain quartic as well as quadratic t_{1u} force constants to represent proper restoring forces in the vicinity of the equilibrium structures.

In the following we present expressions for only the t_{1u} and t_{2g} symmetry coordinates, the (nine) coordinates along which the most significant displacements occur. Since these sets of coordinates are each triply degenerate, they are naturally expressible in terms of x, y, and z components, only the z component of which need be given explicitly here, the others being derivable by inspection. In terms of the numbering scheme of Fig. 1, the t_{1u} stretch and bend and t_{2g} bend coordinates are

$$S_{3z} = 2^{-1/2}(\Delta r_5 - \Delta r_6) , \tag{2.3}$$

$$S_{4z} = 8^{-1/2}(\Delta\alpha_{15} + \Delta\alpha_{25} + \Delta\alpha_{35} + \Delta\alpha_{45}$$
$$- \Delta\alpha_{16} - \Delta\alpha_{26} - \Delta\alpha_{36} - \Delta\alpha_{46}) , \tag{2.4}$$

$$S_{5z} = \tfrac{1}{2}(-\Delta\alpha_{12} + \Delta\alpha_{23} - \Delta\alpha_{34} + \Delta\alpha_{41}) . \tag{2.5}$$

In treating the problem of pseudorotation it is particularly enlightening to transform from the above Cartesian representations to the spherical polar coordinates

$$R_i = (S_{ix}^2 + S_{iy}^2 + S_{iz}^2)^{1/2} , \tag{2.6}$$

$$\theta_i = \arccos(S_{iz}/R_i) , \tag{2.7}$$

and

$$\phi_i = \arctan(S_{iy}/S_{ix}) , \tag{2.8}$$

where i stands for 3, 4, or 5. For the t_{1u} coordinates 3 and 4 the angles θ and ϕ have a clear physical as well as formal significance. As depicted in Fig. 1 (and in much more detail in Fig. 4 of Ref. 5), they correspond exactly to the direction of the xenon lone pair associated with the t_{1u} deformation (in the sense of Gillespie's valence-shell-electron-pair-repulsion theory). This association with stretch as well as bend means that the angular coordinates θ_3, ϕ_3 are strongly correlated with θ_4, ϕ_4 by the potential function though in the following we shall focus on the t_{1u} bend since it involves the largest displacements. Pseudorotation, then, corresponds to a vibrational motion along coordinates θ_4 and ϕ_4, or the sweeping of the lone pair direction around the xenon coordination sphere.

An expression presenting what are presumed to be the most important components of the potential surface in the bending subspace of t_{1u} and t_{2g} is

$$V_{4,5} = \tfrac{1}{2} f_{44}(S_{4x}^2 + S_{4y}^2 + S_{4z}^2) + \tfrac{1}{2} f_{55}(S_{5x}^2 + S_{5y}^2 + S_{5z}^2) + \bar{f}_{4444}(S_{4x}^2 + S_{4y}^2 + S_{4z}^2)^2 + \bar{f}_{4444'4'}(S_{4x}^2 S_{4y}^2 + S_{4y}^2 S_{4z}^2 + S_{4z}^2 S_{4x}^2)$$

$$+ \bar{f}_{445}(S_{4x}S_{4y}S_{5z} + S_{4y}S_{4z}S_{5x} + S_{4z}S_{4x}S_{5y}) + \bar{f}_{4455}[(S_{4x}^2 + S_{4y}^2)S_{5z}^2 + (S_{4y}^2 + S_{4z}^2)S_{5x}^2 + (S_{4z}^2 + S_{4x}^2)S_{5y}^2] + \dots , \tag{2.9}$$

where, as explained above, f_{44} is negative and $\bar{f}_{4444}$ is needed to provide a restoring force toward equilibrium.

Enough points along the potential surface were calculated using basis set I (BAS I)[25] to give rough estimates of the potential constants in Eq. (2.9) corresponding to that basis set. Fewer points were calculated with BAS II,[25] and these were mainly restricted to structures with C_{3v} symmetry. If it were assumed that the potential surface is adequately characterized by Eq. (2.9), it would be possible to express the global minimum in the (S_4, S_5) space in terms of the listed force constants and hence to calculate the corresponding equilibrium structure in this subspace. In fact, the theoretically derived potential surfaces were so highly anharmonic that the pseudopotential energies could not be closely fitted without augmenting Eq. (2.9) by the addition of several more terms. It was plausible to incorporate the potential constants $\bar{f}_{555}$, $\bar{f}_{5555}$, $\bar{f}_{44555}$, and $\bar{f}_{44445}$, and our reported structures and energies of deformation are based on surfaces generated from least-squares fits with those parameters of anharmonicity. Although it is not certain that this set of higher order parameters is the optimum limited set, we believe that the uncertainties associated with these terms did not greatly influence the derivation of the terms listed in Eq. (2.9).

In order to compare the present results with those of Pitzer and Bernstein,[17] it is necessary to consider the following simplification. Pitzer and Bernstein (PB) proposed that the unusual aspects of xenon hexafluoride could be characterized by the deformation energy

$$\overline{V}(R, \theta, \phi) = -aR^2 + bR^4$$
$$- cR^4 \sin^2\theta[\cos^2\theta + \tfrac{1}{4}(\sin^2\theta \sin^2 2\phi)] \tag{2.10}$$

in the t_{1u} bend space, where R, θ, and ϕ represent R_4, θ_4, and ϕ_4 of Eqs. (2.6)–(2.8). The effective potential $\overline{V}(R, \theta, \phi)$ is supposed to express an average over the vibrations of all of the other modes. Although there is a formal correspondence between the PB parameters a, b, and c and their counterparts f_{44}, $\bar{f}_{4444}$, and $\bar{f}_{4444'4'}$ of Eq. (2.9), the strong coupling between the t_{1u} and t_{2g} modes greatly amplifies the deformation energy. For purposes of comparison we constructed a pseudopotential representation of $\overline{V}(R, \theta, \phi)$ for C_{3v} structures by the following simplified approach: We traced a path of nominally steepest descent on the C_{3v} surface $V(R_4, R_5)$ from the $(0, 0)$ point to the minimum to establish energy as a function of R_4. This function was then fitted by the terms in Eq. (2.10) with θ and ϕ assuming values appropriate for C_{3v} symmetry.

III. RESULTS

In Table I are listed orbital energies for XeF_6 as calculated by various methods.[12,23,24,29] Results for several geometric configurations are given. Table II compares the differences between LUMO and HOMO energies in the series XeF_2, XeF_4, and XeF_6 as given by the present calculations and by Basch et al.[24] Clearly evident is the destabilizing effect on the HOMO (lone pair) brought about by increased fluorination as a consequence of the increasing numbers of antibonding interactions imposed on the orbital. As the LUMO–HOMO separation narrows, enhancing the second-order Jahn–Teller effect, the tendency for distortion increases until a spontaneous deformation occurs in the case of the hexafluoride. A section through the HOMO orbital density portraying the lone pair is shown in Fig. 2.

Structural results for XeF_5^* and XeF_6 are presented in Tables III and IV and compared with experiment.[16,27,30,31] The more significant potential constants determined as outlined in Sec. II are listed in Table V, and a graphic representation of the C_{3v} potential surface $V(R_4, R_5)$ is illustrated in Fig. 3.

Supplementary material[32] for XeF_2, XeF_4, XeF_5^*, and XeF_6 has been deposited with the Physics Auxiliary Publication Service.

IV. DISCUSSION

Qualitative aspects of the xenon fluoride structures are reproduced quite well by the present calculations. Although all calculated bond lengths are about 0.1 Å too long, the contractions of 0.031, 0.020, and 0.104 Å in each step along the series XeF_2, XeF_4, XeF_6, and XeF_5^* are in acceptable agreement with the observed values[16,27,30,31,33] (Table IV) of $0.02_7 \pm 0.01$, $0.05_5 \pm 0.01$, and 0.06 ± 0.01 Å, respectively, particularly when allowance is made for the fact that the results for XeF_5^*
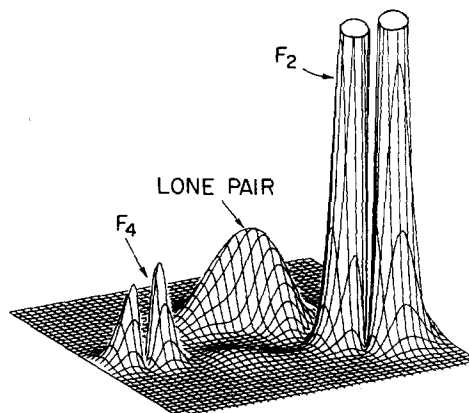

FIG. 2. Electron density plot for XeF_6 of the highest occupied molecular orbital, the "spectroscopic lone pair" (basis set I). The molecule is in a C_{3v} configuration near the theoretically calculated potential minimum. The plane sampled passes through the xenon atom, the lone pair (directed toward the "opened face" 2, 3, 5; Fig. 1), and fluorines 2 and 4; it bisects edges 3, 5 and 1, 6. A localized "chemical lone pair," pointing in the same direction, could be constructed from a linear combination of the a_1 symmetry molecular orbitals.

TABLE I. Orbital energies and ionization energies of XeF_6 as determined by various calculations and experiment. Energies are in hartree.

	Orbital energies						Ionization energies	
	NDDO-2'[a]	SCF[b]	BAS I O_h[c]	BAS II O_h[c]	BAS II O_h[d]	BAS II C_{3v}[d]	MS-$X\alpha$[e]	PES[f]
r(Xe–F) (Å)	1.89	1.89	1.89	1.89	2.02	2.02	1.89	
$6a_{1g}$	−1.80	−1.7408	−1.5573	−1.6264	−1.5715	−1.5957 a_1		
$5t_{1u}$	−1.73	−1.6614	−1.4896	−1.5672	−1.5355	$\{$ −1.5684 e / −1.5056 a_1		
$4e_g$	−1.63	−1.6251	−1.4655	−1.5500	−1.5259	−1.4978 e		
$7a_{1g}$	−1.22	−1.1695	−1.0554	−1.2059	−1.2118	−1.1900 a_1	0.971	0.772(?)
$6t_{1u}$	−0.95	−0.8931	−0.7238	−0.8519	−0.8166	$\{$ −0.8089 e / −0.8034 a_1	0.727	0.735
$3t_{2g}$	−0.74	−0.7536	−0.4682	−0.6531	−0.6349	$\{$ −0.6747 e / −0.6640 a_1	0.579	0.651
$1t_{2u}$	−0.72	−0.7242	−0.4571	−0.6253	−0.6180	$\{$ −0.6566 a_2 / −0.6412 e	0.504	0.629
$7t_{1u}$	−0.71	−0.7183	−0.4477	−0.6093	−0.6061	$\{$ −0.5871 e / −0.5661 a_1	0.504	0.607
$1t_{1g}$	−0.70	−0.7035	−0.4404	−0.6063	−0.6023	$\{$ −0.5797 a_2 / −0.5748 e	0.502	0.588
$5e_g$	−0.66	−0.6653	−0.3499	−0.5492	−0.5072	−0.5023 e	0.562	0.559
$8a_{1g}$[g]	−0.53	−0.4311	−0.1236	−0.3197	−0.3535	−0.3974 a_1	0.420	0.460
$8t_{1u}$[h]	−0.17	−0.0398	0.1843	0.0025	−0.0667	$\{$ −0.0869 a_1 / −0.0192 e	0.295	
E_{VT}[i]		−155.4153	−158.0721	−158.1209	−158.1548			

[a]A zero differential overlap (ZDO) scheme parametrized to reproduce *ab initio* orbital energies, Ref. 29.
[b]Reference 24.
[c]Present work.
[d]Present calculations at the theoretical bond length of minimum energy.
[e]"Transition state" energies, Ref. 23.
[f]Photoelectron spectroscopy, Ref. 12.
[g]HOMO.
[h]LUMO.
[i]E_{VT} is the 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.

compare a bare ion (calculated) with an ion surrounded by conterions (experiment). Moreover, in the case of XeF_6, the calculated difference of 0.086 Å (BAS I) between bonds adjacent to the lone pair and bonds remote from the lone pair in a C_{3v} structure (at minimum energy) agrees with the difference of 0.091 Å found by Hedberg *et al.*[16] For XeF_5^+ an analogous comparison is not quite as favorable. The calculated difference between equatorial and axial bonds is 0.005 Å for the bare ion while the

observed difference[27] in a crystalline environment is +0.03 ± 0.02 Å. It is of some interest to note that the solid-state differences $(r_{eq} - r_{ax})$ in the isoelectronic series SbF_5^{2-}, TeF_5^-, IF_5, and XeF_5^+ are 0.15_9,[34] 0.09_0,[35] 0.05_6,[36] and 0.03_0 Å,[27] respectively, and the vapor phase difference for IF_5 is reported to be 0.034 Å.[37] Evidently, the pronounced elongation of bonds adjacent to the lone pair in the negatively charged members of the series nearly disappear in the cation, and it may be less

TABLE II. Energy differences (LUMO–HOMO) in hartree.

	HF–SCF[a]	r(Xe–F) (Å)	BAS II[b]	r(Xe–F) (Å)	BAS II[b,c]	r(Xe–F) (Å)
XeF_2 ($D_{\infty h}$)	0.519	2.00	0.430	2.01	0.400	2.07
XeF_4 (D_{4h})	0.465	1.95	0.379	1.96	0.343	2.04
XeF_6 (O_h)	0.391	1.89	0.322	1.89	0.287	2.02

[a]Reference 24.
[b]Present work.
[c]Present calculations at theoretical bond lengths of minimum energy.

TABLE III. Structural parameters for XeF$_5^+$ and XeF$_6$.

Species	Parameter	This work[a]	Experiment
XeF$_5^+$	$\angle F_{ax}$–Xe–F_{eq} (deg)	80.75	79.0[b]
	r(Xe–F_{ax}) (Å)	1.909	1.81[b]
	r(Xe–F_{eq}) (Å)	1.914	1.84[b]
XeF$_6$	$\angle C_{3v}$ axis to $F_{open\,face}$ (deg)[c]	79.4	67.5[d]
	$\angle C_{3v}$ axis to $F_{closed\,face}$ (deg)	47.4	52.3[d]

[a]BAS II.
[b]Average values in [XeF$_5^+$]$_2$[PdF$_6^{2-}$], Ref. 27.
[c]Note that the angle between the C_{3v} axis and a bond, for an O_h structure, is 54.74°.
[d]Best C_{3v} static fit to electron diffraction data at 20 °C, Ref. 16. The effect of vibrations on bond angles is small compared with the differences between the pseudopotential and diffraction values.

TABLE V. Potential constants[a] for XeF$_6$.

Type	BAS I	BAS II	PB[b]	Steric[c]	Type	BAS II	Steric[c]
f_{44}	−1.10	−0.52	⋯	0.15	f_{55}	0.61	0.13
$\tilde{f}_{4444}$	0.56	0.67	⋯	0.05			
$\tilde{f}_{4444'4'}$	−0.40	−0.92	⋯	0.11	$\tilde{f}_{445}$	1.96	0.12
−2a	⋯	−1.13	−0.63	⋯	$\tilde{f}_{4455}$	6.28	⋯
$b - \frac{1}{3}c$	⋯	0.26	0.21	⋯			

[a]In mdyn Å. Pseudopotential calculations carried out at 1.8907 Å. See Eqs. (2.9) and (2.10) for definitions.
[b]Reference 17, values inferred from a combination of experimental results interpreted in the context of Eq. (2.10) of the present text.
[c]Calculated solely from the geminal F⋯F nonbonded interactions deduced with the aid of BAS II via the formalism of paper I.

for species in isolation (gas phase) than in solid state environments.

Another pleasing structural result is the close agreement between the calculated (80.8°) and observed (79.2°)[27] F_{eq}–Xe–F_{ax} bond angles in XeF$_5^+$. Here the effect of charge in the series is small as the observed angles[27,34–37] differ by only a degree or two. From the above result we can infer that the stereochemical activity of the lone pair governing the F–Xe–F bond angle presents no intrinsic theoretical difficulty. This fact, together with the satisfactory accounting of XeF$_2$ and XeF$_4$ by the present pseudopotential approach with a minimum basis set, would seem to augur well for the success of a similar treatment of XeF$_6$. Unfortunately, as will be discussed below, this expectation is overoptimistic and xenon hexafluoride turns out to be less well represented by a minimal basis set than were the lower fluorides.

Briefly put, the present calculations are in accord with prior calculations and studies of the electronic spectrum in finding no evidence to support the thermally excited "electronic isomer" interpretation of XeF$_6$.[8] They do, however, yield a result in qualitative agreement with the Bartell–Gavin interpretation[5] of a stereo-

chemically active lone pair on xenon leading to a spontaneous t_{1u} deformation from O_h symmetry. Moreover, again in conformity with the latter interpretation, the deformation is further stabilized by an anharmonic coupling of the t_{2g} mode with the t_{1u}, a circumstance strongly favoring a C_{3v} structure. What is not in harmony with experience[5,16] is that the calculated structures are far too distorted from O_h symmetry, and the stabilization of the deformation is so great that the implied deformation would be static, giving the molecule a permanent dipole moment and low entropy. Displacements from O_h symmetry along a pure t_{1u} bending coordinate were calculated to stabilize the molecule (at the minimum energy C_{3v} configuration) by 28 kcal/mole (BAS I) or 6.8 kcal/mole (BAS II). Pure t_{2g} displacements were destabilizing but, in concert with t_{1u} displacements, they augmented deformation energies considerably, to 92 or 50 kcal/mole (BAS I or BAS II). These values may be compared with the estimate by Bernstein and Pitzer[17] of 5 kcal/mole based upon a variety of empirical observations. All of the above numbers were calculated with the bond lengths fixed at their experimental value[16] of 1.89 Å. If the bonds were increased to their BAS II
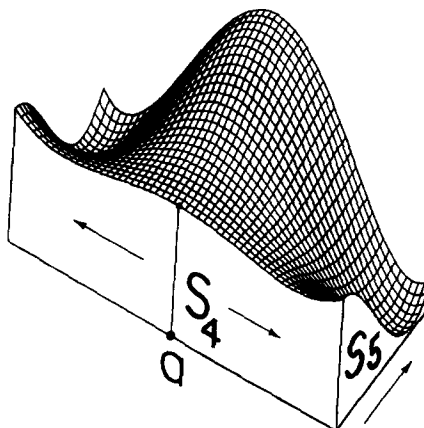
TABLE IV. Xenon–fluorine bond lengths in XeF$_2$, XeF$_4$, XeF$_6$, and XeF$_5^+$.

Symmetry	Molecule	r(Xe–F) (Å) Calculated[a]	r(Xe–F) (Å) Experimental
$D_{\infty h}$	XeF$_2$	2.068	1.977 ± 0.0015[b]
D_{4h}	XeF$_4$	2.037	1.95 ± 0.01[c]
O_h[d]	XeF$_6$	2.017	1.895 ± 0.01[e,f]
C_{4v}	XeF$_5^+$ {axial	1.914	1.81 ± 0.01[e,g]
	{equatorial	1.909	1.84 ± 0.01[e,g]

[a]BAS II.
[b]Reference 30.
[c]Reference 31.
[d]Symmetry imposed in calculations to find the bond length.
[e]Average value.
[f]Reference 16.
[g]Reference 27.

FIG. 3. Potential energy surface for XeF$_6$, basis set II, in the t_{1u} (S_4)–t_{2g} (S_5) subspace along axes carrying the molecule from O_h symmetry at origin "a," to D_{3d} for pure t_{2g}, and C_{3v} for pure t_{1u}. Potential minima are at $R_4 \approx 0.8$ rad, $R_5 \approx 0.7$ rad (oblate t_{2g}).

"theoretical" lengths, the magnitude of the deformation energy fell 60% to a value that is still severalfold too high.

When calculations with basis set I revealed the above symptoms it was natural to inquire to what degree the excessive deformation was related to the fact that fluorine atoms are too small when they are represented by a minimum STO set (BAS I). From symmetry considerations it is apparent that the second-order Jahn–Teller stabilization energy initially increases quadratically with t_{1u} deformations. This means that, if the deformation is checked at a small displacement—as, for example, by steric forces opposing the deformation—the second-order Jahn–Teller stabilization must be small. If the displacement is allowed to increase uncurbed, a considerable stabilization energy can build up. A representation of the potential surface describing this situation is, re-expressing Eq. (2.9),

$$V_{4,5} = \tfrac{1}{2} f_{44} R_4^2 + \bar{f}_{4444} R_4^4 + G_{444'4'} \bar{f}_{444'4'} R_4^4$$

$$+ \tfrac{1}{2} f_{55} R_5^2 + G_{445} \bar{f}_{445} R_4^2 R_5 + G_{4455} \bar{f}_{4455} R_4^2 R_5^2 + \ldots , \quad (4.1)$$

where the coefficients G embody the effects of the orientation of the lone pair on xenon. A negative t_{1u} quadratic constant f_{44} characterizes the second-order Jahn–Teller stabilization. It is augmented by the t_{1u}, t_{2g} coupling constant $\bar{f}_{445}$ and countered by the quartic constants $\bar{f}_{4444}$ and $\bar{f}_{4455}$. Here it is instructive to note that all terms in Eq. (4.1) except for those involving $\bar{f}_{444'4'}$, $\bar{f}_{445}$, and $\bar{f}_{4455}$ are neutral in their influence on the "direction of the lone pair." The net effect of the latter terms is to stabilize the C_{3v} structures preferentially (lone pair in a face of the octahedron), as is apparent from the coefficients G. For C_{3v}, C_{2v}, or C_{4v} structures it can be shown that $G_{444'4'}$ is 1/3, 1/4, or 0, respectively, G_{445} is $3^{-1/2}$, 1/2, or 0, and G_{4455} is 2/3, 1, or 0.

Two lines of evidence show that the excessive distortion of XeF$_6$ implied by the calculations is more deep rooted than the simple underrepresentation of steric forces. First, the second basis set (BAS II) was successful in representing the proper size of fluorine atoms (see paper I), yet it also led to an excessive distortion, though less exaggerated than that yielded by BAS I. Secondly, via the analyses of paper I and Ref. 5, it is possible to estimate the purely steric contributions to the force constants of Eq. (2.9) implied by the deficient set BAS I and by the sterically remedied set BAS II. As shown in Table V, the nonbonded repulsions do, indeed, tend to reduce the leading second-order Jahn–Teller stabilization term (f_{44}), and augment the quartic term opposing deformation. They also, however, augment the anharmonic coupling term ($\bar{f}_{445}$) that strongly stabilizes the deformation. However, the steric contributions are an order of magnitude smaller than the terms they modify and hence are too ineffectual in XeF$_6$—with its large central atom—to be identified as a principal source of trouble.

Although it is premature to speculate at length on the reasons for the deficiencies in the present treatment of XeF$_6$, a few words are in order. The calculated potential energies for the bending deformations of XeF$_2$ and

XeF$_4$ were far superior, though XeF$_4$, through its low e_u force constant, revealed a hint of the trouble to come in XeF$_6$. Decreasing the xenon 5s–fluorine σ overlaps while increasing the separation between 5s and 5p orbital energies would tend to remedy the situation by diminishing the second-order Jahn–Teller activity. Whether inclusion of relativistic corrections, which are in this direction,[38] is important is not yet known. Evidence in Table II comparing the LUMO–HOMO separations of the di-, tetra-, and hexafluorides is suggestive. Trends in the separations are nearly identical for the more flexible all-electron treatment of Basch et al.[24] and the present treatment. Absolute separations are lower for the present calculations, however, presaging an insufficient restoring force for e_u(XeF$_4$) and t_{1u}(XeF$_6$) deformations. Since the separation narrows with increasing fluorination, the trouble increases, becoming severe in the case of XeF$_6$. The principal source of trouble is probably the insufficient flexibility in a minimal basis set.

If, instead of focusing upon the excessive deformation energy of XeF$_6$, we examine individual components of the potential surface, namely, the potential constants in Table V, we find a more favorable comparison between theory and inferences from experiment. To be sure, the improved basis set (BAS II) yields a value for the constant a from Eq. (2.10) appreciably larger than that estimated by Pitzer and Bernstein,[17] in keeping with the aforementioned tendency of the present calculations to make the t_{1u} deformation too large. Still, the deficiency is quantitative, not qualitative. The other parameters of the potential surface for which experimental information is available, namely, $(b - \tfrac{1}{3} c)$ and the lengths of the two different kinds of bonds in XeF$_6$, are in reasonable agreement with experiment. The constant $(b - \tfrac{1}{3} c)$ characterizes the restoring force, averaged over all vibrations except t_{1u} bends, for a C_{3v} structure deformed along a t_{1u} bend. Moreover, as inferred from an electron diffraction analysis,[5] the t_{1u}–t_{2g} coupling is evidently substantial.

On balance, then, even though the present calculations are quantitatively deficient in their representation of a pseudorotating hexafluoride, they reproduce quite well the general features of the potential surface associated with the Bartell–Gavin interpretation. In our opinion, then, the present calculations lend significant new evidence supporting the increasingly accepted picture of a xenon hexafluoride molecule distorted by a stereochemically active lone pair. The calculations err, just as did the original Gillespie–Nyholm VSEPR theory[19] first forecasting a distorted molecule, in making the lone pair too large, larger even than a bond pair in the central-atom coordination sphere. Experience has shown that single determinant SCF calculations based on minimum basis sets cannot be relied upon to yield quantitatively precise bond angles, especially when fluorine atoms are involved. A theoretical investigation of sufficient accuracy to map out the potential surface of XeF$_6$ quantitatively will require a more elaborate computation but one, we believe, that is entirely feasible within the framework of the present pseudopotential technique. Even without the results of such a calculation, however,

the accumulated evidence, taken as a whole, points convincingly to a molecule existing in a single (singlet) ground state and possessing unusual physical properties by virtue of its large amplitude pseudorotation.

ACKNOWLEDGMENTS

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