The Structure of XeF_6 and of Compounds Isoelectronic with It. A Challenge to Computational Chemistry and to the Qualitative Theory of the Chemical Bond

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Abstract: The preference of XeF_6 for either a trigonally distorted or a regular octahedral structure is determined by a delicate balance of several competing factors. A regular octahedron is favored (a) by electron correlation and (b) by the relativistic contraction of the Xe 5*s* orbital. In contrast, higher angular momentum (in particular *f*-type) basis functions on Xe favor a distortion. While earlier SCF or other nonrelativistic calculations were in apparent agreement with experimental evidence for a distorted structure, this has been due to a partial cancellation of errors. The present study contains all-electron calculations as well as calculations of the valence-electrons in an effective core potential. For the former, electron correlation has been included at the MP2 level and relativistic effects by means of direct perturbation theory, for the latter the highest level was CCSD(T) for the treatment of electron correlation, and relativistic effects were simulated by means of a quasirelativistic effective core potential. Both sets of calculations lead to consistent results. These indicate that the "XeF_6-like" XF_6 compounds with light central atoms or ions like ClF_6^- or BrF_6^- prefer the structure of a regular octahedron. The same is true for KrF_6, which is not stable with respect to $Kr + 3F_2$ but probably represents a local minimum. For these light central atoms, electron correlation is decisive for a regular structure, while at Hartree−Fock level, i.e., ignoring correlation effects, the structure of lowest energy is distorted. Regular octahedra are also predicted for systems with very heavy central atoms like RnF_6, AtF_6^-, and PoF_6^{2-}. For these compounds relativistic effects (supported by electron correlation) stabilize the regular octahedron. The situation is more complicated for XeF_6, IF_6^-, and TeF_6^{2-}. Here the strong distortion found at nonrelativistic SCF level is compensated partly, but apparently not completely, by electron correlation and relativistic effects. This results in distorted, fluctuating structures with only little stabilization compared to the regular octahedron. A similar situation holds for SeF_6^{2-}. None of the available simple models of main-group structural chemistry is able to predict or rationalize all of these structures. One inevitably has to use more subtle descriptions.

1. Introduction

There is evidence from experiment,[1−4] that XeF_6 in the gas phase has a fluxional structure based on a trigonally distorted octahedron. Various ions valence-isoelectronic with XeF_6 like ClF_6^-,[5] BrF_6^-,[6,7] or $BiCl_6^{3-}$ [8] were found to exist as regular octahedra in the condensed phase, others like SeF_6^{2-} [7] or IF_6^- [9] as trigonally distorted, still others like $SeCl_6^{2-}$, $SeBr_6^{2-}$, $TeCl_6^{2-}$, $TeBr_6^{2-}$, or TeI_6^{2-} as either octahedral or distorted, depending on the counterion[10,11](see also refs 12 and 13). There were speculations on the structure of this class of compounds before[14] and after[15−18] the first experimental evidence of distortion.

It is now generally accepted that XeF_6 is a molecule with a *stereochemically active lone pair*. Early quantum chemical calculations, essentially of SCF type with small basis sets[19−21] or using effective core potentials,[22] were consistent with this

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interpretation and supported conclusions from experiment, as far as the equilibrium structure of XeF_6 is concerned.

Recent more sophisticated studies[23−27] more or less confirmed the early findings but showed a *large sensitivity of the final result to details of the calculation*. It was found in particular that inclusion of *electron correlation stabilizes the regular octahedron* relative to a distorted structure. In the case of ClF_6^-, a distorted structure was the minimum at the SCF level,[20,25] while with correlation included[25] the O_h geometry became more stable. A similar behavior was found for SeF_6^{2-} and TeF_6^{2-}.[24]

We must conclude that there cannot be a simple theoretical model valid for all systems valence-isoelectronic with XeF_6 (as has been suggested previously[20]) and that a rationalization of the particular structure of XeF_6 cannot be as simple as is often thought. It must rather be based on a concept that is more sophisticated than the simple MO model. This description has to account for electron correlation, as well as for relativistic effects. In particular, the importance of relativistic effects does not appear to have been considered seriously so far. This is surprising, as an *inert pair effect* in a different context[28−30] has been explained in terms of a relativistic stabilization of *s*-type valence AOs (also cf. ref 31).

In this work, we have tried to understand the electronic structure of XeF_6 and related molecules, based on quantum chemical calculations at a state-of-the-art level, complementary to other sophisticated studies.[26,27] In our computations, we have tried to be as little biased as possible, in order to get an accurate theoretical prediction of the equilibrium structure of XeF_6 and of some isoelectronic systems. This requires an understanding of the factors which influence the equilibrium structures.

We will start with a discussion of models for the chemical bond in XeF_6 and related molecules (section 2). After a presentation of the computational methods in section 3, we will report on the results of quantum chemical calculations in increasing order of sophistication, starting with nonrelativistic SCF calculations (section 4) up to quasirelativistic CCSD(T) calculations (section 6). At various levels we compare all-electron calculations with calculations in an effective core potential and find little difference. We shall see that both electron correlation and relativistic effects favor a regular octahedron. In order to arrive at a distorted octahedron for XeF_6 at the highest level of computation, the treatment of electron correlation and the extension of the basis set must be performed in a balanced way.

We are mainly concerned with XeF_6, but we also include valence-isoelectronic molecules or ions in our study, in particular the—experimentally unknown—species with central atoms from the fifth row such as PoF_6^{2-}, AtF_6^-, and RnF_6, for which relativistic effects should play a very important role.

2. Models of Bonding in XeF_6 and Isoelectronic Systems

While for most AB_n molecules or ions various competitive structures are possible, for the special case of AB_6 the octahedral structure with O_h symmetry is highly privileged. It has been pointed out,[32,33] that almost any model predicts an octahedral structure for *normal* AB_6 compounds, and only exceptionally such a structure is not realized. For open-shell states the Jahn-Teller effect[34] may favor deviations from a regular octahedron, for which many examples are known. For simple AB_6 systems in a closed-shell state, nonoctahedral structures are relatively rare, with the XeF_6 ground state probably being the most famous example. Recently, a number of homoleptic d^0 (and d^1) transition-metal complexes with σ-donor ligands, such as MH_6 (M = Cr, Mo, W), $M(CH_3)_6$ (M = W, Mo, Re), or $Zr(CH_3)_6^{2-}$ have stimulated considerable interest.[35] For these species, both theoretical and experimental evidence demonstrate preferences for regular or distorted trigonal prismatic rather than octahedral structures.

In textbooks the C_{3v}-distorted structure of XeF_6 is usually explained in terms of the valence-shell electron-pair repulsion (VSEPR) model, also known as Gillespie−Nyholm model.[36] However, the insight provided by this model is rather limited.[25,37,38] Before applying it, one has to make the following two assumptions:

(a) The molecule can be described in terms of localized two-center XeF bonds and a localized lone pair.

(b) The 5s-AO of Xe is a valence-AO and participates in bonding, in such a way that the 6 XeF bonds as well as the lone pair involve hybrid AOs of Xe to which 5*s* and 5*p*, and possibly 5*d* contribute.

Then one can conclude that seven electron pairs have to be accommodated in the outer sphere of Xe, with the lone pair requiring more space, such that a structure with an "active lone pair" results. The essential issue is not the application of the VSEPR model but rather the justification of the underlying assumptions, i.e., whether the lone pair is stereochemically active or not. The rationalization of the distorted structure in terms of the VSEPR model is hence almost a tautology.

There are two somewhat more sophisticated but still much oversimplified models of bonding in XeF_6. One is that of three-center four-electron FXeF bonds[39,40] and the other is qualitative MO theory making use of the symmetry properties of the molecular orbitals.[12,14,17,41−43] In the former model only the 5*p*-

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AOs of Xe are regarded as valence-AOs, while 5*s* is taken as part of the core. This model is consistent with the structure of a regular octahedron and a stereochemically inactive lone pair, as realized experimentally for several ions valence-isoelectronic with XeF_6, such as condensed-phase ClF_6^- or BrF_6^-.[5−7] This model is more realistic than the VSEPR model insofar as no assumptions on hybridization and in particular on localized two-center bonds are made. However, the model does not consider the participation of the 5*s*-AO of Xe in the bonding. An approach to the hypervalent bond due to Musher[50] is essentially a paraphrase of the three-center four-electron bond model.

The most satisfactory of the elementary models is that of qualitative MO theory.[12,14,17,41−43] Starting from the AOs 5*s* and 5*p* of Xe and 2*p* of F one gets the following valence MOs of σ-type for an octahedral structure

$$\text{bonding: } 1a_{1g},\ 1t_{1u}$$

$$\text{nonbonding: } 1e_g$$

$$\text{antibonding: } 2a_{1g},\ 2t_{1u}$$

Eight electrons from Xe and six electrons from F have to be distributed among the valence-MOs, which leads to the 14-valence-electron configuration

$$1a_{1g}^2 1t_{1u}^2 1e_g^2 2a_{1g}^2$$

This may be compared with the ground configuration of systems with two electrons less, which are valence-isoelectronic with SF_6. For these $2a_{1g}$ is unoccupied, and it is obvious that both 3*s* and 3*p* (in SF_6) participate in bonding, namely 3*s* in $1a_{1g}$ and 3*p* in $1t_{1u}$. In systems like XeF_6 both $1a_{1g}$ and $2a_{1g}$ are doubly occupied. The former MO is 5*s*-bonding and the latter 5*s*-antibonding. If a bonding as well as an antibonding MO is doubly occupied, this is essentially equivalent to no bonding at all. At this level an a posteriori justification of the three-center four-electron bond model involving only 5*p* and only 12 valence electrons comes out.[41]

How can one allow for distortion in this MO model? If 5*s* and 5*p* participate in bonding to a comparable extent, then the antibonding MOs $2a_{1g}$ (the HOMO) and $2t_{1u}$ (the LUMO) are close in energy. A mixing of these MOs may lower the overall energy. Such a mixing is prohibited by symmetry in the O_h structure (HOMO and LUMO belong to different symmetry species) but allowed in a distorted structure, e.g., of C_{3v} type where HOMO and LUMO belong to the same symmetry species (a_1). Another way of phrasing this is to say that distortion allows a participation of 5*s* in bonding. Of course, distortion is also accompanied by some energy raising effects,[25] such that the extent of distortion is the result of a delicate balance. Stabilization is also possible by means of a distortion to C_{2v}-symmetry (the stereochemically active lone pair then squeezes into an edge rather than into a plane of the octahedron).

The energetic stabilization of a molecule in a *degenerate* ground state by distortion to a structure of lower symmetry is referred to as Jahn-Teller effect,[34] which occurs whenever there is a *Jahn-Teller-active mode*. In analogy, a stabilization by symmetry lowering of a molecule in a *nondegenerate* ground state is sometimes called a second-order Jahn-Teller effect.[44] It can be interpreted via an increased HOMO−LUMO splitting, due to a HOMO−LUMO interaction which is only possible in a distorted structure.

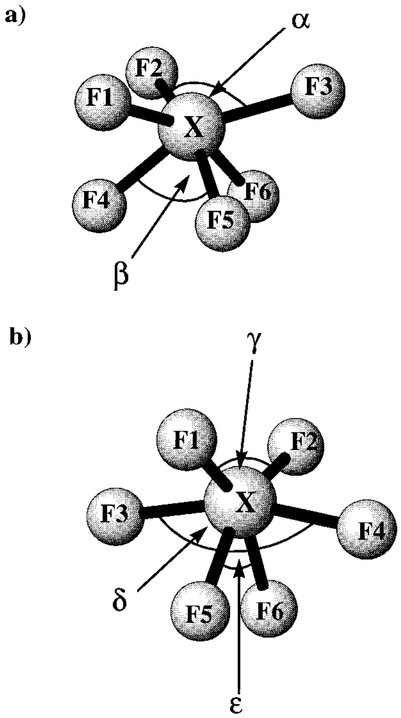

Figure 1. Atom labels for XF_6: (a) C_{3v} and (b) C_{2v}.

The concept of a second-order Jahn-Teller effect, or synonymously a pseudo-Jahn-Teller effect, goes back to Öpik and Pryce[45] (see also refs 46 and 47). The topic has been reviewed.[48,49] The distortion from a regular structure is actually only a minor aspect of the Jahn-Teller or pseudo-Jahn-Teller effects. More important is the fact that two potential surfaces intersect (for the Jahn-Teller effect) or come very close to each other (for the pseudo-Jahn-Teller effect). Thus, the Born−Oppenheimer approximation breaks down, and nuclear motions such as vibrations have to be described in terms of (at least) two electronic states.

In the case of a pseudo-Jahn-Teller effect, the ground state energy has a saddle-point at the structure of high symmetry and the energy is lowered by a *pseudo-Jahn-Teller active mode*. While a pseudo-Jahn-Teller effect is always associated with a saddle-point on the potential energy surface, not every saddle-point is necessarily related to a pseudo-Jahn-Teller effect. In a rather popular notation,[12,42,43] even the bent equilibrium structure of H_2O is regarded as due to a second-order Jahn-Teller effect. If one gives this concept such a broad meaning, which we do not encourage, the distortion of XeF_6 may be referred to as a manifestation of a pseudo-Jahn-Teller effect. Actually the terms pseudo-Jahn-Teller effect or second-order Jahn-Teller effect have been used in different meaning by different authors, while there appears hardly any controversy about the meaning of the genuine Jahn-Teller effect.

The qualitative MO models also allow some conclusions both as to the localizability and the polarity of the bonds in XeF_6 and related molecules. In fact, in the three-center four-electron bond model as well as in the full MO model both bonding and nonbonding MOs are occupied, the latter with only ligand

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contributions. This implies a highly ionic (semipolar) character with the negative charge on F.

In a strict sense, the MO description in terms of three-center four-electron bonds is not compatible with an alternative description in terms of localized two-electron bonds (as, e.g., required for the VSEPR model). This incompatibility is very pronounced for purely covalent bonds but less so for highly polar bonds. In the limit of purely ionic bonds all bonding MOs are localized on the ligands and are hence a fortiori two-center bonds. Application of a standard localization criterion, e.g., that ascribed to Boys,[51] to a construction of localized MOs in XeF_6 and related molecules results in LMOs that do not look much different from *ordinary* polar two-center LMOs.

One can extend the qualitative MO theory by considering π-type bonding. The (doubly occupied) π-AOs of the F atoms form nonbonding linear combinations of the species t_{1g}, t_{1u}, t_{2g}, and t_{2u}. These can become bonding if they find an unoccupied low-lying MO on Xe as a partner (see later). If one regards the MOs engaged in π-bonding as valence MOs, one has to deal with more than 14 valence electrons, confirming the absence of a unique definition of the number of valence electrons in compounds like XeF_6.

Qualitative MO theory is usually formulated in terms of a minimal valence basis. This means that for XeF_6 the theory is built upon the 5*s*- and 5*p*-AOs of Xe and a $2p\sigma$-AO of each F atom as we have just done. An improved description involves deformed AOs and this deformation can be accounted for by augmenting the basis by "polarization functions", usually of functions with an angular momentum quantum number *l* increased by one, i.e., additional *p*- and *d*-functions for Xe and *d*-functions for F. It turns out (see below) that even *f*-functions are very important for XeF_6. This is somewhat unexpected, since *secondary* polarization functions (with *l* augmented by more than one unit) usually have only a small effect at the MO level. Note that the *f*-functions are not needed to deform the 4*d*-AOs. These are practically not involved in bonding, and even omitted as part of the core in ECP calculations. One aspect of the importance of *f*-functions in XeF_6 is that 4*f*-AOs are relatively low in energy, anticipating that in the row of the periodic system starting after Xe 4*f*-AOs become occupied in the atomic ground states. There is also some effect of *f*-AOs in Kr and even Cl^- (see later), but it is much smaller.

Polarization functions can serve to stabilize XeF_6 or related species even in the O_h structure, e.g., *d*-AOs on F can make the σ-nonbonding $1e_g$-MO bonding and can make the nonbonding π-type t_{2g}-MO back-bonding, while *f*-AOs on Xe stabilize the σ-MOs $1t_{1u}$ and the π-MOs of t_{1u} and t_{2u} type. If one distorts the molecule to a C_{3v} structure, one only has three different irreducible representations (a_1, a_2, and *e*) instead of 10 irreducible representations for O_h. The valence configuration $1a_{1g}^2 1t_{1u}^2 1e_g^2 2a_{1g}^2$ is then changed to $1a_1^2 2a_1^2 1e^2 2e^2 3a_1^2$ and *d*-type AOs on Xe ($a_1 + 2e$) as well as *f*-type AOs on Xe ($2a_1 + a_2 + 2e$) can mix into almost all valence-MOs, and there is much more flexibility to lower the energy than in the O_h structure. Polarization functions are thus expected to favor the distorted structures. It is not so easy to see qualitatively why *f*-functions on Xe are so effective in this respect, as is found numerically (see section 4).

If one leaves this qualitative MO model and tries a quantitative treatment within the MO context, by performing a standard ab-initio MO-SCF calculation, one finds a distorted structure, in agreement with these qualitative arguments (see later for details). However, this is not the final truth, and there are two reasons for this.

(a) The MO model, or in its quantitative form the SCF approximation, is not exact, since it only takes care of the average interaction of the electrons, not of the fact that the motion of the electrons is correlated.

(b) Xe is a rather heavy element for which relativistic effects are by far not negligible.[28−30]

As to electron correlation, it is convenient to distinguish between *dynamical* and *nondynamical* correlation.[52] Dynamical correlation has to do with the short-range repulsion of the electrons, while the origin of nondynamical correlation effects is near-degeneracy of energy levels. In the latter case, a description of the respective states by means of a single Slater determinant is poor, and one has to use a linear combination of a few Slater determinants as reference function.

A particularly important nondynamical correlation contribution in XeF_6 is due to the strong interaction between the $1a_{1g}^2 1t_{1g}^2 e_g^2 2a_{1g}^2$ ground valence configuration and the doubly excited configuration $1a_{1g}^2 1t_{1g}^2 1e_g^2 1t_{1u}^2$ of the same overall symmetry $^1A_{1g}$ (for O_h geometry). There is obviously a competition between the stabilization of the ground state by admixing of a $2a_{1g}^2 \rightarrow 1t_{1u}^2$ double excitation (which is allowed even in O_h geometry) and by an admixing of a $2a_{1g}^2 \rightarrow 2a_{1g}1t_{1u}$ single excitation (which is prohibited in O_h geometry and only possible for lower symmetry). In ignoring the possibility of a double excitation (i.e., in an SCF calculation) one overestimates the importance of single excitations and hence of the distortion. This is nicely illustrated by the example of ClF_6^- for which we compare in section 5 an ordinary SCF-calculation with a multiconfiguration-SCF-configuration, in which both the valence configurations $1a_{1g}^2 1t_{1g}^2 e_g^2 2a_{1g}^2$ and $1a_{1g}^2 1t_{1g}^2 1e_g^2 1t_{1u}^2$ are considered. If the energetic stabilization by double excitation is taken care of, the importance of stabilization by single excitations (which requires distortion) is much reduced.

The main relativistic effects are

(a) scalar relativistic effects

(b) spin-orbit interactions.

For a closed-shell molecule like XeF_6, to the leading relativistic order $O(c^{-2})$ only scalar relativistic effects contribute, while spin-orbit effects first show up to $O(c^{-4})$. We therefore expect (*Z* is only modestly large for Xe) that we have to care mainly for scalar relativistic effects. It is easy to understand qualitatively that scalar relativistic effects favor the O_h structure of XeF_6 and related molecules. The main reason is that the difference in energy and in radial extent between the 5*s*- and 5*p*-AOs of Xe is increased due to relativistic effects.[28−30] This reduces the mixing between 5*s* and 5*p* (hybridization) and makes 5*s* more *inert* (stereochemically inactive). The relativistic stabilization of the 6*s*-AO is so strong in Rn that RnF_6 almost becomes a regular octahedron already at quasirelativistic SCF level (see section 6). The same is true for AtF_6^- and PoF_6^{2-}.

To be complete in the review of previous approaches, we should also mention an application of exchange perturbation theory by L. Jansen et al.,[53] which has probably only historical interest as well as a study of XeF_6 in terms of the structure-

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resonance paradigm by Herndon.[54] Gutsev and Boldyrev have used X_α calculations to interpret the photoelectron spectra of XeF_6.[55] Calculations by Malli et al. including electron correlation and relativistic effects have been published for XeF_2 and XeF_4[56] and have been announced for XeF_6[57] but only for a regular octahedron. The same holds for quasirelativistic ECP calculations on RnF_6 by Dolg et al.[58] A state-of-the-art study of the potential surface of XeF_2 in ground and excited states has recently been published by Marian and Perić.[59]

3. Computational Methods and Basis Sets

All-Electron Calculations. For the light atoms F, Cl, Ar, Se, Br, and Kr, split-valence basis sets of *triple* ζ quality in the valence shell, augmented by one set of polarization functions (TZVP)[60] have been used. For the elements Te, I, and Xe, a 21*s*17*p*12*d* basis set has been taken from a compilation by Huzinaga and Klobukowski,[61] contracted to 15*s*13*p*8*d*, and augmented by one set of *f*-functions with exponent 0.370511 for Te, 0.393976 for I, and 0.420027 for Xe. The *d*-set is already large enough, so no additional *d*-functions are necessary. Following a procedure proposed by Crawford et al.,[26] the *f*-exponents have been obtained by minimizing the Hartree–Fock energy of the octahedral hexafluorides XeF_6, IF_6^-, and TeF_6^{2-}. These will be referred to as the "standard" basis sets. For XeF_6 we have in addition performed calculations with the somewhat smaller basis of Crawford et al.[26] and with a still smaller basis without *f* functions, namely a Dunning set[62] in the contraction (6,9×1/4,7×1/3,5×1) for Xe and a (8*s*,4*p*) Huzinaga basis for F in the contraction (5,1,1,1/3,1) augmented by a diffuse *p*-function ($\eta = 0.074$) and a *d*-function ($\eta = 1.4$). This is the basis referred to as "without *f*" in the text and the tables. For the MC-SCF calculations on ClF_6^-, the following Huzinaga-type basis sets have been used. Cl: (12*s*,9*p*) in the contraction (6,6×1/4,5×1) augmented by two *d*-sets with η=0.4 and 1.6 ; F: (9*s*,5*p*) in the contraction (5,4×1/3,1,1) augmented by one *d*-set ($\eta = 1.0$). Additional SCF and MP2 calculations on ClF_6^- with basis sets containing more polarization functions will be mentioned in the text.

ECP Calculations. We have used both the quasirelativistic and the nonrelativistic eight-valence-electron ECPs of Nicklass et al. for Xe and Kr.[63] Quasirelativistic ECPs were employed for F, Cl, Br, I, Se, Te,[64] quasi- and nonrelativistic ECPs for Rn, At, and Po,[65] with a (5*s*5*p*1*d*)/[3*s*3*p*1*d*] valence basis set (including diffuse functions) for F,[66] and (4*s*4*p*1*d*)/[2*s*2*p*1*d*] for the other elements.[64–66] This moderate size of ECP valence basis sets will be denoted "A" in the following (for both quasirelativistic and nonrelativistic ECPs). Basis A is the only ECP basis used for the entire set of molecules and ions, as structure optimizations with ECPs *and f*-functions in the basis did not allow the use of analytical gradients, due to program limitations. Numerical ECP optimizations with larger valence basis sets have been carried out for selected examples, i.e., for XeF_6, IF_6^-, and RnF_6. For iodine, the extended valence basis (with quasirelativistic ECP) involved a (6*s*6*p*)/[3*s*3*p*] set[67] augmented by the three most diffuse *d*-functions and the *f*-function taken from the all-electron basis (vide supra). For radon, the 4*s*4*p* valence bases for both quasirelativistic and nonrelativistic ECP[65] were used in a (2,2×1/2,2×1) contraction and augmented by three *d*-functions ($\eta = 0.5432808$, 0.29491399, 0.160 095 3)[68] and one *f*-function (optimized as described above, $\eta = 0.422$). These extended ECP valence basis sets will be denoted "C". Several different sets of polarization functions were compared for Xe. The smallest basis including *d*-AOs ("A") consisted of a 6*s*6*p* valence basis[63] contracted to (3,3×1/3,3×1) and augmented by one set of *d*-functions (the same size of basis was used for Kr).[63] Basis A without *d*-AOs on Xe will be termed "A_0". More accurate calculations on XeF_6 (bases "B" through "D") used a (2,4×1/2,4×1) contraction and replaced the single *d*-set by three sets of *d*-functions.[63] Basis "C" included one ($\eta = 0.5157$),[63] basis "D" two ($\eta = 0.5157$, 0.1719) additional sets of *f*-functions on Xe. When we refer to the basis "with *f*" in the ECP context we usually mean basis C, while "without *f*" indicates basis A.

The all-electron calculations at the Hartree–Fock and density functional level have been performed with the TURBOMOLE package[69] on top of which a density functional program has been implemented,[70] and which has also been extended to calculate leading-order relativistic corrections[71] using the framework of direct perturbation theory.[72] Higher-order relativistic calculations[72] are currently only possible for single-point energies and have been done for selected geometries with a new program developed in our laboratory.[72] The all-electron MP2 geometry optimizations have been performed with the program MPGRAD[74] which is also a part of the TURBOMOLE package. HF, MP2, and DFT structure optimizations with ECPs have been carried out with the Gaussian92/DFT and Gaussian94 programs.[75] Coupled-cluster calculations used the MOLPRO92 and MOLPRO94 programs.[76]

4. Nonrelativistic SCF-Calculations

Most previous calculations on XeF_6 and valence-isoelectronic molecules, including ours,[25] were done at SCF level, either by nonrelativistic all-electron calculations or with effective core potentials (ECP), also called pseudopotentials (nonrelativistic or quasirelativistic). Our present results of nonrelativistic structure optimizations are collected in Table 1 for O_h symmetry, in Tables 2 and 3 for C_{3v} symmetry, and are available as

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Table 1. Bond Lengths r(XF) in Å for O_h Symmetry[a]

	SCF			MP2			
	all-el.	ECP(NR)	ECP(QR)	all-el.	ECP(NR)	ECP(QR)	DFT-[f] all-el.
ArF_6	1.753	1.759	1.755	*b*	*b*	*b*	1.905
KrF_6	1.807	1.812	1.808	1.972	*b*	*b*	1.919
XeF_6[c,d]	1.930	1.950	1.943	1.985	2.024	2.030	
XeF_6[d,e]	1.898	1.912	1.905	1.952	1.976	1.971	1.985 (1.980)
RnF_6[c]		2.025	2.003		2.097	2.077	
RnF_6[e]		1.981	1.963		2.033	2.017	
ClF_6^-	1.756		1.762	1.850		1.863	1.860
BrF_6^-	1.848		1.844	1.910		1.909	1.934
IF_6^- [c]			1.997			2.047	
IF_6^- [e]	1.973		1.975	2.004		2.012	2.040 (2.033)
AtF_6^-		2.091	2.078		2.141	2.128	
SeF_6^{2-}	1.950		1.970	1.982		2.011	2.013
TeF_6^{2-}	2.092		2.113	2.103		2.147	2.141 (2.133)
PoF_6^{2-}		2.215	2.158		2.247	2.189	

[a] Unless indicated otherwise, all-electron results with standard basis (with *f*-functions), and ECP-results with basis-A (without *f*-functions) are given. [b] Dissociation at this level. [c] Basis without *f*-AOs on X. [d] A CCSD/basis-C (QR-ECP) optimization gives a Xe−F distance of 1.948 Å. [e] Basis with *f*-AOs on X. [f] Relativistic DFT results in parentheses.

Table 2. Bond Lengths in Å for C_{3v} Symmetry[a]

	SCF			MP2			
	all-el.	ECP(NR)	ECP(QR)	all-el.	ECP(NR)	ECP(QR)	DFT[h]
ArF_6 r(X-F1)	*b*			*c*			*b*
r(X-F4)	*b*			*c*			*b*
KrF_6 r(X-F1)	1.721	1.735	*b*	*b*	*c*	*c*	*b*
r(X-F4)	1.877	1.879	*b*	*b*	*c*	*c*	*b*
XeF_6[d,e] r(X-F1)	1.830	1.857	1.869	1.910	*b*	*b*	*b* (*b*)
r(X-F4)	1.963	1.984	1.988	2.006	*b*	*b*	*b* (*b*)
XeF_6[e,f] r(X-F1)	1.792	1.798	1.808	1.856	(1.872[g])	*b*	*b* (*b*)
r(X-F4)	1.925	1.936	1.945	1.972	(1.993[g])	*b*	*b* (*b*)
RnF_6[d] r(X-F1)		1.937	*b*		(2.015[g])	*b*	
r(X-F4)		2.040	*b*		(2.106[g])	*b*	
RnF_6[f] r(X-F1)		1.879	1.901		1.937	*b*	
r(X-F4)		1.984	2.000		2.034	*b*	
ClF_6^- r(X-F1)	1.603		1.654	*b*		*b*	*b*
r(X-F4)	1.908		1.879	*b*		*b*	*b*
BrF_6^- r(X-F1)	1.709		1.755	*b*		*b*	*b*
r(X-F4)	1.971		1.935	*b*		*b*	*b*
IF_6^- [d] r(X-F1)			1.899			*b*	
r(X-F4)			2.065			*b*	
IF_6^- [f] r(X-F1)	1.833		1.855	1.888		*b*	1.965 (*b*)
r(X-F4)	2.027		2.043	2.052		*b*	2.092 (*b*)
AtF_6^- r(X-F1)		1.959	*b*		2.028	*b*	
r(X-F4)		2.118	*b*		2.170	*b*	
SeF_6^{2-} r(X-F1)	1.732		1.819	*b*		*b*	
r(X-F4)	2.180		2.136	*b*		*b*	
TeF_6^{2-} r(X-F1)	1.892		1.969	1.947		*b*	2.035 (*b*)
r(X-F4)	2.209		2.237	2.202		*b*	2.227 (*b*)
PoF_6^{2-} r(X-F1)		2.045	*b*		2.118	*b*	
r(X-F4)		2.304	*b*		2.334	*b*	

[a] See Figure 1a for atomic labels. Unless indicated otherwise, all-electron results with standard basis (with *f*-functions) and ECP-results with basis-A (without *f*-functions) are given. [b] Optimization converges to O_h structure at this level. [c] Dissociation at this level. [d] Basis without *f*-functions on X. [e] A CCSD/basis-C (QR-ECP) optimization gives Xe−F distances of 1.867 and 1.982 Å. [f] Basis with *f*-functions on X. [g] Optimization converged to C_{3v} structure above O_h structure, see text. [h] Relativistic DFT results in parentheses.

supporting information for C_{2v} symmetry. Binding energies with respect to X + 3F_2 are given in Table 4, whereas energy differences between distorted and regular octahedral structures are shown in Table 5. Table 6 displays the total energies of the all-electron calculations for O_h geometry at SCF and MP2-level, to allow a comparison of the quality of our calculations to that of previous ones.

Imposing O_h symmetry, one finds an energetic minimum even for ArF_6 and KrF_6. From the energies of the reaction (Table 4)

$$X + 3F_2 \rightarrow XF_6$$

one sees that ArF_6 and KrF_6 are quite unstable with respect to

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Table 3. Bond Angles in Degrees for C_{3v} Symmetry[a]

		SCF			MP2		
	all-el.	ECP(NR)	ECP(QR)	all-el.	ECP(NR)	ECP(QR)	DFT[h]
KrF_6 α	84.9	84.4	*b*	*b*	*c*	*c*	*b*
β	104.5	106.1	*b*	*b*	*c*	*c*	*b*
XeF_6[d,e] α	80.4	81.2	81.7	81.2	*b*	*b*	*b*
β	114.9	114.7	112.4	111.7	*b*	*b*	*b*
XeF_6[e,f] α	81.0	80.6	81.1	80.8	(80.5[g])	*b*	*b* (*b*)
β	114.9	115.3	113.7	112.8	(112.9[g])	*b*	*b* (*b*)
RnF_6[d] α		79.7	*b*		(79.9[g])	*b*	
β		116.4	*b*		(113.3[g])	*b*	
RnF_6[f] α		79.2	81.2		79.2	*b*	
β		116.8	110.1		115.5	*b*	
ClF_6^- α	86.7		86.2	*b*		*b*	*b*
β	103.9		102.3	*b*		*b*	*b*
BrF_6^- α	84.9		84.9	*b*		*b*	*b*
β	106.9		103.4	*b*		*b*	*b*
IF_6^- [d] α			81.9			*b*	
β			111.0			*b*	
IF_6^- [f] α	81.3		81.7	81.1		*b*	82.8 (*b*)
β	114.9		112.6	113.0		*b*	105.7 (*b*)
AtF_6^- α		79.6	*b*		79.7	*b*	
β		116.5	*b*		114.4	*b*	
SeF_6^{2-} α	85.6		84.6	*b*		*b*	
β	107.7		105.0	*b*		*b*	
TeF_6^{2-} α	81.9		82.6	81.7		*b*	82.1 (*b*)
β	114.1		108.5	112.1		*b*	104.3 (*b*)
PoF_6^{2-} α		80.6	*b*		81.2	*b*	
β		114.2	*b*		110.2	*b*	

[a] See Figure 1a for definition of the angles. Unless indicated otherwise, all-electron results with standard basis (with *f*-functions), and ECP-results with basis-A (without *f*-functions) are given. [b] Optimization converges to O_h structure at this level. [c] Dissociation at this level. [d] Basis without *f*-functions on X. [e] A CCSD/basis-C (QR-ECP) optimization gives F−Xe−F angles of 81.3 and 111.9 deg. [f] Basis with *f*-functions on X. [g] Optimization converged to C_{3v} structure above O_h structure, see text. [h] Relativistic DFT results in parentheses.

Table 4. Binding Energies (in kJ/mol) of XF_6 with Respect to $X + 3F_2$[a]

		SCF			MP2		
	all-el.	ECP(NR)	ECP(QR)	all-el.	ECP(NR)	ECP(QR)	DFT all-el.[e]
ArF_6	1651.0	1700.5	1600.6	*b*	*b*	*b*	630.3
KrF_6	1008.5	947.8	946.0	337.7	*b*	*b*	204.3
XeF_6[c]	238.7	264.4	373.2	−44.5	−88.1	−79.9	
XeF_6[d]	38.6	−23.7	63.9	−241.2	−249.6	−247.0	−304.4 (−305.4)
RnF_6[c]		−16.4	128.5		−269.7	−262.9	
RnF_6[d]		−410.3	−188.3		−573.1	−491.3	
ClF_6^-	15.8		−30.5	−480.1		−546.2	−562.9
BrF_6^-	−372.4		−445.6	−748.3		−828.0	−834.2
IF_6^- [c]			−869.8			−1126.0	
IF_6^- [d]	−1000.5		−1019.7	−1203.3		−1201.6	−1157.1 (−1169.0)
AtF_6^-		−1039.1	−958.1		−1205.3	−1215.7	
SeF_6^{2-}	−1653.9	−1711.7		−1850.3		−1961.7	−1826.4
TeF_6^{2-}	−1825.0		−2053.6	−1971.0		−2234.6	−1836.5 (−1851.0)
PoF_6^{2-}		−1981.2	−2117.5		−2112.5	−2275.3	

[a] Results for most stable structure at a given level. Unless indicated otherwise, all-electron results with standard basis (with *f*-functions), and ECP-results with basis-A (without *f*-functions) are given. Positive numbers indicate that the molecule is less stable than the fragments. [b] Dissociation at this level. [c] Basis without *f*-AOs on X. [d] Basis with *f*-AOs on X. [e] Relativistic DFT results in parentheses.

$X + 3F_2$ at SCF level, but even XeF_6 is unstable, while all the singly and doubly negative ions are stable (with the exception of ClF_6^-, which is very slightly unbound). For the doubly charged ions the binding energies in Table 4 are not too meaningful, since the corresponding atomic dianions are not stable at Hartree−Fock level (one eigenvalue of the Fock matrix is positive). However, the ions SeF_6^{2-} and TeF_6^{2-} have only negative Hartree−Fock eigenvalues.

Thus, the results for the molecular ions as such are meaningful.

We have also performed calculations of SF_6^{2-} but did not include them in the tables, as it is not clear whether the isolated ion SF_6^{2-} is stable with regard to electron detachment. We found a slightly positive eigenvalue of the Fock matrix at the Hartree−Fock minimum, while at the MP2-structure the highest eigenvalue of the Fock matrix was slightly negative.

Table 1 indicates very good agreement between the O_h structures from all-electron and ECP calculations, at least for the systems with light central atoms such as Ar, Kr, Cl^-, Br^-, for which the basis sets in the two kinds of calculations are comparable. In XeF_6, the effect of *f*-AOs in the Xe basis is to reduce the bond length by ∼3 pm and to increase the binding energy considerably (both for all-electron and for ECP calculations). To be sure that the *f*-AOs on Xe are decisive, we have performed calculations (not documented here) with two basis sets that only differ in the presence and absence of *f*-AOs and duplicated practically the difference between the standard basis and the small basis.

To get a feeling for the relative importance of polarization functions for heavy and light central atoms we have also varied the *d*- and *f*-parts in ClF_6^-. The results for single point calculations at the geometries in Tables 1−3 are not documented

Table 5. Energy Differences between C_{3v} (C_{2v}) and O_h Structures in kJ/mol[a]

	SCF			MP2			
	all-el.	ECP(NR)	ECP(QR)	all-el.	ECP(NR)	ECP(QR)	DFT all-el.
KrF_6	9.4 (7.6)	11.9 (9.1)	*b*	*b*	*c*	*c*	
XeF_6[e]	113.8 (109.0)	115.2 (110.1)	44.8 (40.5)	*b*	*b*	*b*	
XeF_6[f]	192.8 (176.8)	197.8 (183.6)	103.8 (93.7)	9.1(-2.6)	−1.5[d] (−7.8[d])	*b*	*b* (*b*)[g]
RnF_6[e]		153.7 (143.3)	*b*		−17.0[d] (−19.9[d])	*b*	
RnF_6[f]		240.4 (216.3)	17.3 (12.2)		63.7 (49.4)	*b*	
ClF_6^-	49.6 (48.9)		16.7 (15.9)	*b*		*b*	*b*
BrF_6^-	42.3 (38.9)		9.3 (8.0)	*b*		*b*	*b*
IF_6^- [e]			31.0 (27.7)			*b*	
IF_6^- [f]	167.2 (152.7)		66.6 (58.9)	36.8(27.4)		*b*	2.2(0.6)[g]
AtF_6^-		156.0 (142.5)	*b*		26.9 (21.3)	*b*	
SeF_6^{2-}	72.1(69.6)		26.0 (25.2)	*b*		*b*	
TeF_6^{2-}	133.0(125.6)		25.1 (23.3)	40.3(34.9)		*b*	3.5(2.4)[g]
PoF_6^{2-}		72.6 (66.8)	*b*		13.5 (11.3)	*b*	

[a] Positive numbers indicate the distorted structure to be more stable than O_h. Unless indicated otherwise, all-electron results with standard basis (with *f*-functions), and ECP-results with basis-A (without *f*-functions) are given. [b] Optimization converges to O_h structure at this level. [c] Dissociation at this level. [d] Optimizations in C_{3v} and C_{2v} symmetry converge to distorted structures above O_h structure, see text. [e] Basis without *f*-AOs on X. [f] Basis with *f*-AOs on X. [g] The relativistic DFT calculations give a preference for an octahedral structure, also for IF_6^- and TeF_6^{2-}.

in the tables but can be summarized as follows. For a basis with one *d* and no *f* on Cl, the C_{3v}-structure (on SCF level) is lower by 49.6 kJ/mol, with three *d* and no *f* this difference is increased to 56.3 kJ/mol, with one *d* and one *f* to 63.3 and with three *d* and one *f* to 68.3 kJ/mol. These additional polarization functions have also a similar effect on the absolute energies of the O_h structure. They play a role, but a much smaller one than in XeF_6. Without *d*-AOs (and *f*-AOs) on Cl, the C_{3v} structure lies only 5.7 kJ/mol below the O_h structure, so without *d*-AOs there is practically no stabilization of the C_{3v} relative to the O_h structure.

ArF_6 exhibits only an O_h minimum. The energy gain upon distortion to C_{3v} (Table 5) is very small for KrF_6, rather small for ClF_6^- and BrF_6^-, but quite large for the fourth-row and the fifth-row species (intermediate for SeF_6^{2-}). The optimized C_{2v} structures lie energetically generally between O_h and C_{3v} but closer to the latter. The inversion barriers from C_{3v} via C_{2v} to C_{3v} are only a few kJ/mol, implying that pseudorotation via this route should be easy.

For the distorted structures, there is also rough agreement between the all-electron and ECP results. The agreement improves considerably for bond lengths when comparing results with similar basis sets, in particular when *f*-functions are included in both all-electron and ECP valence basis sets (cf. entries for XeF_6 and IF_6^- in Tables 1−3, and supporting information). In these cases, bond angles appear to be less sensitive to the inclusion of *f*-AOs than bond lengths (also cf. ECP results for RnF_6). The computed structural parameters for the C_{2v}-transition state of XeF_6 (available as supporting information) are consistent with those of the distorted XeF_6-unit found very recently as part of a solid-state $Xe_2F_{13}^-$ anion.[77]

The agreement of nonrelativistic SCF calculations and experiment on a preference for a distorted XeF_6 structure is, as we shall see, a mere coincidence and is due to a compensation of various errors. In fact, for the simple systems ClF_6^- and BrF_6^- the SCF results do not agree with experiment (which of course has been done in the condensed phase).

5. Nonrelativistic Calculations Including Electron Correlation

We have used various approaches to include electron correlation effects.

(a) MP2 (Møller-Plesset perturbation theory to second order): This was done both at all-electron level and with ECPs. All electrons have been correlated in the all-electron calculations. The MP2 results are included in Tables 1−6.

Table 6. Total Energies (in E_h) of All-Electron Calculations[a] in the Standard Basis for the O_h Structures of the XF_6 Species

molecule	SCF	MP2
Xe[b]	−7 232.129 381	−7 233. 126 393
F_2	−198.764 542	−199.223 962
ArF_6	−1 122.467 655	
KrF_6	−3 347.908 142	−3 349.832 565
XeF_6[c]	−7 828.334 908	−7 830.886 588
ClF_6^-	−1 055.824 056	−1 057.575 914
BrF_6^-	−3 168.899 671	−3 170.726 385
IF_6^-	−7 514.677 046	−7 517.176 316
SeF_6^{2-}	−2 996.526 308	−2 998.296 416
TeF_6^{2-}	−7 208.602 542	−7 211.067 287

[a] SCF and MP2 energies at the respective minima (with O_h constraint for the XF_6 species). [b] This value has been obtained for the contracted basis of ref 61, the uncontracted basis yields −7 232.132 034 E_h, for the basis of ref 26, the contracted and uncontracted values are −7 231.724 437 E_h and −7 232.138 101 E_h, respectively. The Hartree−Fock limit has been estimated as −7 232.153 E_h (Fraga, S.; Saxena, K. M. S.; and Karwowski, J. Handbook of Atomic Data; Elsevier: Amsterdam 1976). [c] Reference values −7 828.106 1 E_h and −7 830.305 8 E_h ref 26, note that in these calculations a much smaller basis for F was used.

Table 7. MC-SCF Results[a] for ClF_6^-

	E_{MC-SCF}[b] [E_h]	r_1 [Å]	r_2 [Å]	α [deg]	β [deg]	E_{SCF}[c] [E_h]
O_h	−1 055.814 810	1.750	1.750	90	90	−1 055.772 500
C_{3v}	−1 055.823 624	1.594	1.895	87.0	102.8	−1 055.790 355

[a] Basis sets described in section 3, angles on figure 1. [b] MC-SCF energy at the respective minimum, characterized by the subsequent coordinates. [c] SCF energy at the MC-SCF minimum.

(b) A multiconfiguration (MC-SCF) calculation, taking care of the two-most important configurations ...$(a_{1g})^2$ and ...$(t_{1u})^2$: This was only done for ClF_6^- in an all-electron context and is displayed in Table 7.

(c) Coupled-cluster (CC) calculations with single and double substitutions (CCSD) and with singles, doubles, and an approximate treatment of triples (CCSD(T)): These calculations were done only for XeF_6, together with ECPs (section 7).

(d) Density functional (DFT) calculations, to be explained in more detail later: All-electron DFT results are also included in Tables 1−5. DFT calculations combined with ECPs will be mentioned in section 7.

As expected, at MP2 level all XF_6 systems are stabilized with respect to X + $3F_2$, as compared to SCF (Table 4). XeF_6 is now bound. Only for ArF_6 one no longer finds a minimum.

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[77] Ellern, A.; Mahjoub, A. R.; Seppelt, K. *Angew. Chem.* **1996**, *108*, 1198. *Angew. Chem., Int. Ed. Engl.* **1996,** *35*, 1105.

ClF_6^-, KrF_6 (the latter only in the all-electron calculation, at ECP/basis-A level it dissociates), BrF_6^-, and SeF_6^- now prefer regular octahedra (Table 7).

In the case of ClF_6^- the stabilization of the O_h structure is so strong that even with increased basis sets by more polarization functions as discussed in the previous section, the O_h structure is by far lowest. The difference between the MP2 energies at the SCF minima for O_h and C_{3v}-structure is 122.8 kJ/mol for the standard basis (1*d*, no *f* on Cl) and 105.0 kJ/mol for a basis with 3*d* and 1*f*.

AtF_6^- and PoF_6^{2-} remain distorted at MP2 level. With XeF_6, IF_6^-, TeF_6^{2-}, and RnF_6 the situation is more complicated. For basis sets without *f*-functions at the central atom, the most stable structure has O_h symmetry (for RnF_6, distorted C_{3v} and C_{2v} arrangements are also obtained but are higher in energy than the O_h structure). With the larger all-electron basis sets (with *f*-functions), XeF_6, IF_6^-, and TeF_6^{2-} become distorted at nonrelativistic MP2 level. However, note the very small energy differences in the case of XeF_6 (cf. Table 5). With the Crawford[26] basis, which is somewhat smaller than our standard all-electron basis, or with nonrelativistic ECP and basis C, one obtains distorted structures for XeF_6, which however are slightly above the O_h minimum (similar to the ECP/basis-A results for RnF_6, see above). Crawford et al.[26] missed to locate the C_{3v} minimum, since they performed no geometry optimization at MP2 level. Nonrelativistic ECP/basis-C results for RnF_6 favor a distortion.

In order to understand why the inclusion of electron correlation stabilizes the octahedral structure, we have checked whether the mechanism outlined in section 2 is correct. We therefore performed a two-configuration calculation with the two relevant configurations for ClF_6^- in order to take care of the typical nondynamical correlation related to near-degeneracy. The results (see Table 7) were, in part, unexpected. While at SCF level the O_h structure is a saddle point, it becomes a minimum at MC-SCF level. However, the most stable structure for both SCF and MC-SCF has C_{3v} symmetry. While this lies below the best O_h structure by ~47 kJ/mol at SCF level, it is only lower by ~23 kJ/mol in an MC-SCF calculation. The inclusion of doubly excited configurations $(a_{1g})^2 \rightarrow (t_{1u})^2$ obviously stabilizes O_h relative to C_{3v}. However, there must be additional correlation effects that stabilize O_h as well, such that at MP2 level (and probably with correlation treatments of higher sophistication as well) the lowest minimum has O_h structure.

The bond lengths in ClF_6^- differ very little between SCF and MC-SCF, while the MP2 bond lengths differ much from SCF or MC-SCF. There is obviously a correlation effect on the bond lenghts which is, of course, not unexpected and not included in the just-mentioned MC-SCF approach, namely the left−right correlation within the ClF bonds. This is known to increase the bond lengths with respect to SCF.

Density functional (DFT) calculations provide a popular way to simulate correlation effects. We have performed all-electron DFT calculations with a gradient-corrected ("nonlocal") density functional consisting of the local density approximation in the parametrization of Vosko et al.,[78] Becke's gradient correction to exchange,[79] and Perdew's 1986 gradient correction to the correlation functional .[80] The results obtained with the same basis sets as the genuine ab-initio calculations are also included Tables 1−5.

Both equilibrium structures and energy differences from DFT calculations are rather close to the MP2 results (except for KrF_6, which anyhow is not bound with respect to Kr + $3F_2$). Generally, DFT favors the regular octahedron even more strongly than does MP2. While at MP2 level with the large all-electron basis XeF_6 comes out distorted, it is a regular octahedron at DFT level. Among the molecules studied at all-electron DFT level, only IF_6^- and TeF_6^{2-} are distorted. However, the stabilization by distortion is very small (Table 5).

6. Relativistic and Quasirelativistic Calculations

Curiously enough, in no previous work relativistic effects were regarded as important in the context of the equilibrium structure of XeF_6. We have used two approaches to include relativistic effects:

(a) Stationary direct perturbation theory (S-DPT),[72] at the Hartree−Fock level and in combination with DFT, as well as with MP2.

(b) Simulation of scalar relativistic effects by a quasirelativistic effective core potential (at all levels of including electron correlation, up to CCSD(T); cf. section 7). SCF and MP2 results with quasirelativistic ECPs are included in Tables 1−5.

Let us start with the all-electron calculations. We have first evaluated the relativistic corrections by means of direct perturbation theory up to $O(c^{-6})$ to the SCF energy for SCF-optimized O_h and C_{3v} structures. The results are shown in Table 8. The relativistic corrections are not only rather large (~216 Hartree), they also significantly depend on the geometry. As a result, the C_{3v} structure lies ~190 kJ/mol below the O_h structure at nonrelativistic SCF, but only ~96 kJ/mol lower than O_h at relativistic SCF level. Relativistic effects significantly stabilize the O_h relative to the C_{3v} structure. However, it does not matter much for the relative energies to which order in c^{-1} one goes. Inclusion of the contributions of $O(c^{-4})$ or $O(c^{-6})$ lowers the total energy by ~16 and ~1 Hartree, respectively, but has no significant effect on the relative energy. Even the crudest relativistic approximation, the use of the energy independent Cowan−Griffin operator[81] (i.e., only velocity mass and Darwin terms at one-electron level) yields practically the same relative energy.

Relativity has also a slight effect on the geometrical parameters. Minimization of the O_h and C_{3v} structure of XeF_6 at the Cowan-Griffin level gives the second set of data in Table 8. The effect on the energy difference is small. The best estimate for the O_h/C_{3v} difference at relativistic SCF level is 97 kJ/mol (to be compared with the nonrelativistic value of 193 kJ/mol).

For closed shell states such as the ground state of XeF_6 the leading relativistic correction to $O(c^{-2})$ of the Hartree−Fock energy is entirely determined by scalar relativistic effects, spin-orbit interaction only enters to $O(c^{-4})$. We can hence conclude, at least at this level, that spin-orbit effects only play a minor role.

The relativistic effect at all-electron level is in good agreement with that from calculations with a nonrelativistic and a quasirelativistic ECP, as seen from Tables 1−5. In fact, with basis C the nonrelativistic-ECP SCF energy difference between O_h and C_{3v} is 197.8 kJ/mol, and the quasirelativistic ECP result is 103.8 kJ/mol. This gives us confidence in the reliability of the ECP calculations on other molecules or ions and in the higher-level treatments of electron correlation in section 7.

Our program does not yet allow to evaluate the relativistic correction to the correlation energy in an all-electron MP2-calculation. However we can treat both electron correlation at MP2 level and relativistic effects by DPT, assuming them to

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[81] Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. A* **1976**, *66*, 1010. Martin, R. L. *J. Phys. Chem.* **1983**, *87*, 750.

Table 8. Relativistic Corrections to the All-Electron SCF- and MP2-Energy of the O_h and C_{3v} Structures of XeF_6[a–c]

geometries		E_0	$E_0 + c^{-2} E_{CG}$	$E_0 + c^{-2} E_2$	$E_0 + c^{-2} E_2 + c^{-4} E_4$	$E_0 + c^{-2} E_2 + c^{-4} E_4 + c^{-6} E_6$
optimized at SCF-level with “standard” basis set	O_h	−7 828.334 908	−8 026.303 772	−8 027.944 961	−8 043.395 900	−8 044.463 108
	C_{3v}	−7 828.408 333	−8 026.339 362	−8 027.980 793	−8 043.432 434	−8 044.499 530
	Δ_{SCF}	192.84	93.47	94.11	95.95	95.66
optimized at SCF-CG-level with “standard” basis set	O_h	−7 828.334 760	−8 026.303 944	−8 027.945 135	−8 043.396 399	−8 044.463 609
	C_{3v}	−7 828.406 842	−8 026.340 642	−8 027.982 053	−8 043.433 498	−8 044.500 585
	Δ_{SCF}	189.31	96.38	96.96	97.43	97.11
optimized at MP2-level with “standard” basis set	O_h	−7 830.886 588	−8 028.853 023	−8 030.494 204	−8 045.942 500	−8 047.009 700
	C_{3v}	−7 830.890 043	−8 028.827 080	−8 030.468 451	−8 045.917 711	−8 046.984 765
	Δ_{MP2}	9.07	−68.14	−67.63	−65.10	−65.50

[a] To calculate the relativistic corrections on MP2-level additivity of relativistic and correlation corrections is assumed and E_0 is chosen as the MP2-energy, while the relativistic corrections are calculated at SCF-level. [b] E_0 is the nonrelativistic energy, E_2, E_4, and E_6 are the relativistic corrections obtained by means of direct perturbation theory, E_{CG} is the energy corrections of Cowan−Griffin, which is an approximation to E_2. [c] Energies in Hartree, energy differences between O_h and C_{3v} in kJ/mol.

Table 9. C_{3v} (C_{2v}) vs O_h Energy Differences (kJ mol^{-1}) for XeF_6 at Various Computational Levels[a]

basis	HF	MP2	CCSD	CCSD(T)
NR				
A	+110.0 (+96.4)	−55.2 (−54.4)	+12.9 (+9.6)	−17.7 (−18.5)
C	+166.7 (+144.9)	+2.0 (−5.8)	+73.0 (+60.4)	+38.1 (+28.5)
QR				
A_0[b]	+65.8 (+49.2)	−75.2 (−79.2)	+16.8 (−25.4)	+37.8 (−44.2)
A	+44.4 (+38.9)	−95.5 (−86.2)	−37.4 (−32.9)	−61.4 (−54.5)
B	+52.0 (+46.1)	−84.4 (−75.9)	−25.7 (−22.1)	−49.6 (−43.6)
C	+86.3 (+73.3)	−37.1 (−36.1)	+18.8 (+14.7)	−4.8 (−6.1)
D	+95.5 (+82.1)	−40.2 (−39.3)	+20.6 (+16.3)	−6.6 (−8.2)

[a] Results with ECPs. At CCSD/basis-C (with quasirelativistic ECP) optimized structures. Positive values indicate a preference for the less symmetrical structure. [b] Xe *d*-function removed from basis A.

be additive. This combined effect is shown in the third set of data on Table 8. While at the nonrelativistic MP2-level the distorted C_{3v} structure is lower by 9 kJ/mol, at the combined level the O_h structure is preferred by ∼65 kJ/mol. These values can be compared with ∼2 and ∼40 kJ/mol from ECP calculations for quasirelativistic CCSD geometries (see Table 9). The agreement between all-electron and ECP-values is not perfect. However, there is only *one* minimum at relativistic MP2 level (of O_h symmetry) but two minima at nonrelativistic SCF level. Thus, the relativistic C_{3v} energies correspond to points on the repulsive slope of the potential energy surface and have no direct meaning.

The main message of this section is that relativistic effects generally stabilize the regular octahedron. This stabilization is marginal for the light central atoms, moderate for Xe, I, Te, and pronounced for Rn, At, and Po. Note in particular that the equilibrium structure of RnF_6, AtF_6^-, and PoF_6^{2-} is that of a regular octahedron already at the SCF/basis-A level (RnF_6 is still slightly distorted with basis C), provided that relativistic effects are simulated by a quasirelativistic ECP. For these systems relativistic effects are more important than electron correlation. Upon neglect of relativity but inclusion of correlation at the MP2/basis-A level, AtF_6^- and and PoF_6^{2-} are the only two systems that distort to C_{3v}. RnF_6 exhibits a C_{3v} local minimum at this level, but the O_h structure is lower in energy (Table 5). Relativistic effects are also evident from inspection of C_{3v} vs O_h energy differences for TeF_6^{2-} obtained in nonrelativistic all-electron and in quasirelativistic ECP calculations by Klobukowski.[24] This has apparently not been noted before.

Table 2 shows that the level of relativistic density functional theory gives the structure of a regular octahedron for all molecules studied by all-electron calculations, even for IF_6^- and TeF_6^{2-}, which were distorted at nonrelativistic DFT level. At MP2 level with quasirelativistic ECPs, all molecules of this study have the structure of a regular octahedron, including XeF_6. It is of course disappointing that at this reasonably high level of sophistication, XeF_6 comes out as a regular octahedron, in disagreement with experiment. In recent studies with inclusion of electron correlation by means of coupled-cluster and CI calculations,[26,27] a C_{3v} distorted structure has been obtained for XeF_6. However, in these studies relativistic effects were neglected. Since relativity favors a regular octahedron, the good agreement with experiment must be regarded as fortuitous (see below).

7. Improved Treatment of XeF_6

We have tried to perform the best calculation that is possible for XeF_6 at present. Such a calculation should

(a) use a basis that is sufficiently close to saturation in the valence part

(b) be at the highest standard level of electron correlation

(c) be at least quasirelativistic

(d) be feasible on the computer installations available.

Criterion (d) excludes all-electron calculations, but ECPs can be regarded as sufficiently reliable (see above). The use of ECPs also facilitates the quasirelativistic framework. We have hence decided to perform CCSD and CCSD(T) calculations with a quasirelativistic pseudopotential and various basis sets. C_{3v} (C_{2v}) vs O_h relative energies are collected in Table 9. They have been obtained at structures optimized at CCSD/basis-C level with quasirelativistic Xe ECP (at this level, a distorted structure is favored, see Table 9).

Upon going from HF to MP2, there is an appreciable stabilization of the O_h vs the C_{3v} structure by roughly 120−140 kJ/mol. However, MP2 overshoots correlation effects since on going from MP2 to CCSD this stabilization is reduced by approximately 60 kJ/mol. CCSD in turn underestimates correlation effects, and in going from CCSD to CCSD(T) the O_h structure gains again 20−30 kJ/mol (C_{2v} vs O_h energy differences behave similarly, see numbers in parentheses).

Extension of the basis set, in particular the addition of *f*-functions on Xe, stabilizes the C_{3v}-structure considerably relative to O_h. While, e.g., with basis A and nonrelativistic ECP, the O_h structure is lowest at CCSD(T) level, with the large bases C or D, the distorted structure is preferred (upper part of Table 9). Note that our CCSD and CCSD(T) C_{3v} vs O_h energy differences of 73.0 and 38.1 kJ/mol obtained with basis C and nonrelativistic ECP agree well with the all-electron CCSD (63.1 kJ/mol) and CCSD(T) (24.7 kJ/mol) results of Lee and Taylor.[27]

If one now takes care of relativistic effects by means of a quasirelativistic ECP (lower part of Table 9), the O_h structure is strongly stabilized with respect to a C_{3v} structure. Consequently, at MP2 level the O_h structure is lowest for all basis sets. At CCSD level the distorted structure is lowest, provided one uses either of the large basis sets C,D. However, at

Table 10. C_{3v} vs O_h Energy Differences (kJ mol^{-1}) for XeF_6 at Various DFT Levels[a]

basis	BLYP	B3LYP	BHLYP
NR			
C	−13.4	+24.4	+84.7
QR			
A_0[b]	−79.1	−46.1	+1.6
A	−93.3	−62.9	−17.7
B	−84.9	−54.2	−8.7
C	−52.3	−19.3	+29.6
D	−52.1	−19.1	+29.4

[a] Results with ECPs. At CCSD/basis-C (with quasirelativistic ECP) optimized structures. Positive values indicate a preference for the C_3v structure. [b] Xe *d*-function removed from basis A.

CCSD(T) level even with the largest basis ("D") the O_h structure has the lowest energy.

Thus, our best calculation, i.e., CCSD(T) with the large basis D and a quasirelativistic pseudopotential, predicts the O_h structure to be lower in energy by 6.6 kJ/mol as compared to the C_{3v} structure. This is a very small difference, probably within the limits of reliability of our approach (the sign might already change when using structures optimized at CCSD(T) rather than at CCSD level).

One can now speculate what would have to be done to get the distorted structure lower in an even better calculation. Further increase of the basis may slightly favor the C_{3v} structure. Since there is a significant change from CCSD to CCSD(T), one may argue that convergence with respect to the hierarchy of the cluster expansion has not yet been reached. However, it is hard to guess into which direction the next-higher level, say CCSDT(Q) would go. A more explicit study of relativistic effects may also have to be considered, in particular the role of spin-orbit effects and of mixed terms between relativity and correlation, possibly the Breit interaction should be included. Also, the approximations involved in the ECP approach may have some small effect on the energetic ordering between the C_{3v} and the O_h structure. Finally, changes in zero-point energy of the other degrees of freedom are likely to matter.

Most of these possible corrections probably go in different directions, and it would not make too much sense to take care of them, unless this is done in a balanced way. We leave the reader with the message that at our highest computational level possible at present, one cannot decide whether the equilibrium structure of XeF_6 is a regular or a distorted octahedron. There are too many competitive effects. Anyway, the difference in the energies of the two structures appears to be hardly larger than ~10 kJ/mol. This also shows clearly that a simple pictorial explanation of the observed distorted structure is not possible.

Table 10 gives DFT results obtained with the same ECPs and valence basis sets as well as the same CCSD/basis-C(QR) optimized structures as the data in Table 9. Using a gradient-corrected exchange-correlation functional (BLYP),[79,82] the results are rather similar to those obtained at the MP2 level with the corresponding ECPs and basis sets, i.e., the stability of the O_h structure is overestimated considerably (cf. all-electron DFT calculations in section 5). With hybrid HF/DFT functionals (which have become popular during the past few years), the results depend strongly on how much exact Hartree−Fock exchange is mixed in. Thus, results with the BHLYP functional[83] (i.e., with 50% Hartree−Fock exchange) resemble those obtained at CCSD level with the same basis. Results obtained with the B3LYP functional[84] (involving 20% Hartree−Fock exchange) are closer to the CCSD(T) results in terms of energy differences. Clearly, to choose a functional to reproduce experiment without any rigorous theoretical justification is not a satisfactory approach. To be sincere, the present state of density-functional theory does not allow a reliable prediction for the structural preferences of XeF_6, even less so than is possible with ab initio methods in the proper sense.

8. Conclusions

The structure of XeF_6 is controlled by a very delicate balance of various competing effects, and no simple rationalization of it is possible. Let us now again have a look at the systems valence-isoelectronic with XeF_6, which we have studied here only at a lower level of sophistication than XeF_6 itself. However, most of these species appear to be less problematic.

For ions with light central atoms such as ClF_6^- and BrF_6^-, the energy gain by distortion at the SCF level is so small that electron correlation establishes a preference for the O_h structures. Relativity (via quasirelativistic pseudopotentials) changes very little and an increase of the basis has apparently no chance to invert this trend. Thus, for these ions improved calculations are not expected to make qualitative changes.

For molecules with very heavy central atoms, i.e., RnF_6, AtF_6^-, and PoF_6^{2-}, relativistic effects reduce the energy gain from distortion tremendously, already at the SCF level. Electron correlation gives an extra preference to O_h structures. Increase of the basis may lead to a relative stabilization of C_{3v} over O_h but is hardly expected to overcompensate relativity and correlation. Thus, again we do not expect improved calculations to change the qualitative prediction of regular octahedral structures for these species (note that early powder X-ray diffraction work on salts containing PoX_6^{2-} anions, with X = Cl, Br, I, generally gave cubic structures, consistent with undistorted octahedra).[11]

Critical are hence those compounds with a central atom from the fourth row, i.e., XeF_6, IF_6^-, and TeF_6^{2-} (and to some extent SeF_6^{2-}). Here the energy lowering from O_h to C_{3v} at nonrelativistic SCF level is relatively large, and the stabilization of the O_h structure by electron correlation and relativistic effects is about as large. Thus, there is a delicate balance between relativity, electron correlation, and basis-set effects. This makes it so hard to predict whether the equilibrium structure is a regular or a distorted octahedron. As distorted and regular structures are rather close in energy, it is not surprising that small perturbations may decide in favor of one or the other. This appears to be the case, e.g., for $TeCl_6^{2-}$ depending on the counterion[10] and thus possibly on crystal packing effects.

It may be worthwhile to extend the present study by considering other ligands than F, namely Cl and Br. So far we have not worried about this.

In summary, for X from the second, the third (except for SeF_6^{2-}), or the fifth row, 14-valence-electron XF_6 systems (here we do not count nonbonding electrons on fluorine) prefer regular octahedral structures. Only for X from the fourth row, and probably SeF_6^{2-}, a distorted octahedron is competitive. Note that at the nonrelativistic SCF level, a steady increase of the preference for a distorted structure would be predicted from the second to the fifth row. This is probably due to reduced ligand−ligand repulsions and larger polarizabilities of the heavier central atoms.

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(82) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(83) Hybrid HF/DFT functional with 50% HF exchange, as proposed by Becke (Becke, A. D. *J. Phys. Chem.* **1993**, *98*, 1372) but as implemented in the Gaussian92/DFT program (ref 75), together with the LYP correlation functional (ref 82).

(84) Becke's three-parameter HF/DFT hybrid functional (Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648) but in the G92/DFT implementation (ref 75).

We have seen in this study that XeF_6 and its valence-isoelectronic ions are a major challenge to computational chemistry, which implies that an unbalanced calculation may fortuitously give the right answer. Interestingly, as soon as a given theoretical level favors a C_{3v} minimum, the bond angles (see Table 3) agree well with those estimated experimentally,[1−4] even though the energy differences to an O_h structure may differ widely. This has also been noted by Klobukowski in the context of different basis sets at SCF level.[24] Angular structures of C_{2v} stationary points change somewhat more (see supporting information).

This series of compounds is also a challenge to the qualitative interpretation of molecular structure. We have shown that of the various model approaches discussed in section 2 of this paper each has some merit. However, all of them fail to explain why XeF_6 is a distorted octahedron while most of the ions valence-isoelectronic with it are not. In particular, XeF_6 is not a manifestation of the VSEPR model, and hardly a straightforward case of a second-order Jahn-Teller effect.

At this point one may ask what the simple qualitative models are supposed to simulate. One possible answer is that they should simulate nonrelativistic Hartree−Fock theory. At the Hartree−Fock level, all molecules of this study are distorted and have stereochemically active electron pairs, in agreement with the prediction of models based on orbital interaction (or on electron pair repulsion). However, reality is different. This is a warning to overestimate the reliability of models based on orbital interactions alone.

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Note Added in Proof. After submitting the final version of this paper, we became aware that in their study of RnF_6,[58] Dolg et al. included some calculations in C_{3v} symmetry. In agreement with our results they found that a regular octahedral structure is favored by relativistic effects, whereas a distorted structure was found at the MP2 level with nonrelativistic ECPs.

Supporting Information Available: Table A (bond lengths for C_{2v} symmetry) and Table B (bond angles for C_{2v} symmetry) (4 pages). See any current masthead page for ordering and Internet access instructions.

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