

Hypervalence: A Useful Concept or One that Should be Gracefully Retired?

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Supplementary Material

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1. General MO description of p-block element compounds EX_n

Figure S1 is a general MO energy-level diagram for compounds of the form EX_n that have a formal electron count of more than 8 and where E is a p-block element that is less electronegative than X. It is based on a ligand group orbital (LGO) approach featuring symmetry-allowed interactions. It is assumed that:

- (a) the involvement of d-orbitals is negligible;
- (b) s-p mixing does not fundamentally change the energy order of the MOs;
- (c) π -bonding interactions arising from negative hyperconjugation can be ignored at this level of approximation.

Figure S1 represents a fusion of the features that emerge from the analysis of the MO diagrams for individual EX_n species that are given in Section 3.

In Figure S1, the frontier molecular orbitals for EX_n are collected into 5 bands. The number of LGOs generated for EX_n will be n , of which x will not have a symmetry match with any of the s or p orbitals on E and so will remain non-bonding orbitals that are localised solely on the X ligands. As a consequence, there will be $n - x$ orbitals that are E–X bonding. One of the bonding MOs will be formed from the interaction of the s orbital on E with the totally symmetric LGO on X and will have symmetry label a , a_1 , a_g , a_{1g} , a' , or a_1' according to the symmetry of the s orbital within the point group for EX_n ; the antibonding counterpart of this bonding orbital is labelled " a_1 " in Figure S1. The energy of " a_1 " will depend on the efficiency of the orbital overlap between the s orbital on E and the appropriate LGO. The more diffuse the s orbital on E, the lower the energy of the antibonding combination " a_1 " and therefore, the energy of " a_1 " would be expected to become lower, as the periodic group is descended. The energy of " a_1 " is assumed to fall between the original s and p atomic orbital energies of E and will thus be predominantly localised on the central atom E; the electrons that occupy " a_1 " can therefore be considered to have the characteristics of a "lone pair" on E. If the n in EX_n is less than 4, there will be $4 - n$ unused p orbitals on E which will become non-bonding orbitals localised on E. Finally, there will be a set of $n - 1$ unoccupied E–X antibonding orbitals derived from the combination of p orbitals on the element E and the LGOs of the same symmetry.

Stable electron configurations occur when the orbitals are filled up to a level where a closed shell is obtained and the HOMO-LUMO gap is significantly large. This happens, as indicated in Figure S1, at 3 levels, when the orbitals are filled, up to and including:

- (1) Level 1, i.e., the E–X bonding orbitals and any non-bonding orbitals on X (Type I species);
- (2) Level 2, the " a_1 " orbital (Type II species);
- (3) Level 3, the non-bonding orbitals on E (Type III species).

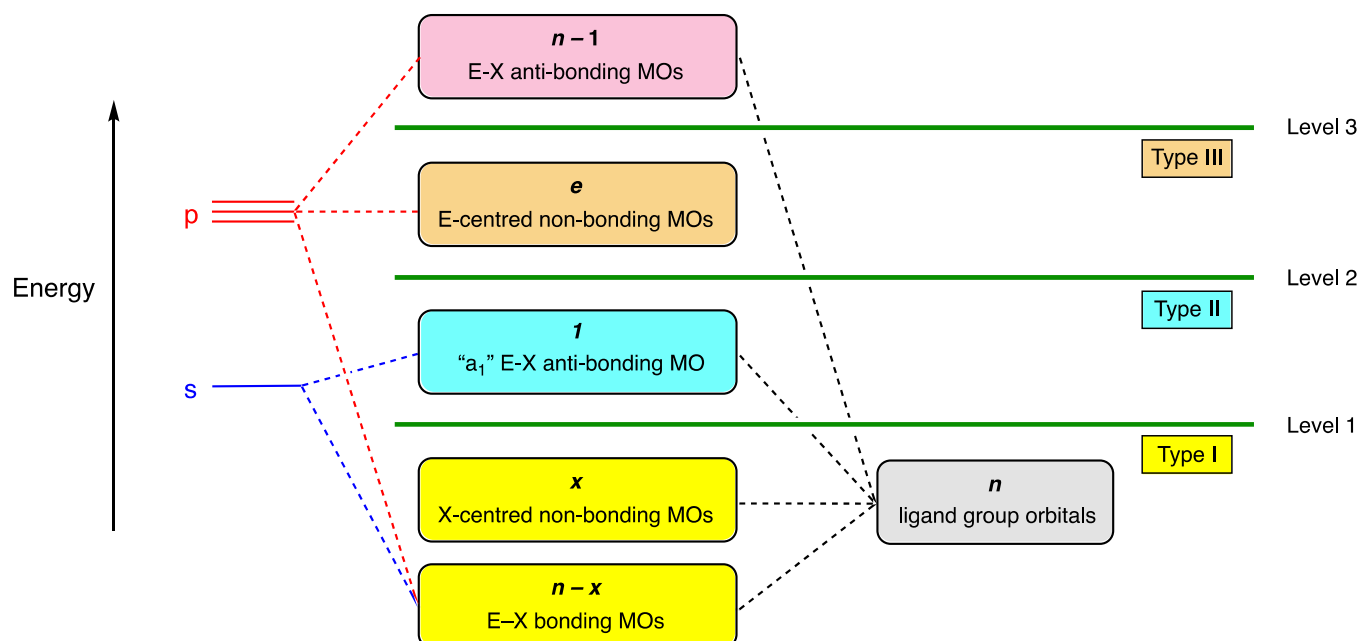


Figure S1 A generic MO diagram for p-block compounds EX_n where X is more electronegative than E, the formal electron count is greater than 8, d-orbital involvement is assumed to be negligible, and no account is taken of s-p mixing or π -bonding effects. The number of pairs of electrons that can occupy each of the bands is $n-x$, x , 1, e and $n-1$ respectively. Types I-III and Levels 1-3 are defined in the text.

2. Further discussion of MO diagrams for some EF_n compounds

In the main article, the MO diagrams for PF_5 , SF_6 , IF_3 and XeF_4 are presented and there is some discussion of how these diagrams correlate with classical concepts such as valence and lone pairs. From a teaching perspective, these correlations can be easily visualised if the MO diagrams are modified so that the electrons that are contributed by E and F are delineated. In Figs. S2-S4, the electrons contributed by E are represented by magenta arrows and the electrons contributed by F are represented by black arrows. This is a formalism, since the electrons in the MOs are not localised exclusively on either E or F.

2.1 Lone pairs and valence in IF_3 and XeF_4

The advantage of codifying the electrons in the manner described above is that it makes obvious (especially for teaching purposes) the valency of E and the electrons that can be classified as "lone pairs" on E. For example, from the MO diagrams in Figures S2 and S3, it is clear that in IF_3 , iodine is

trivalent and has two lone pairs and in XeF_4 , xenon is tetravalent and also has two lone pairs. These interpretations correlate well with the traditional Lewis structures of these molecules.

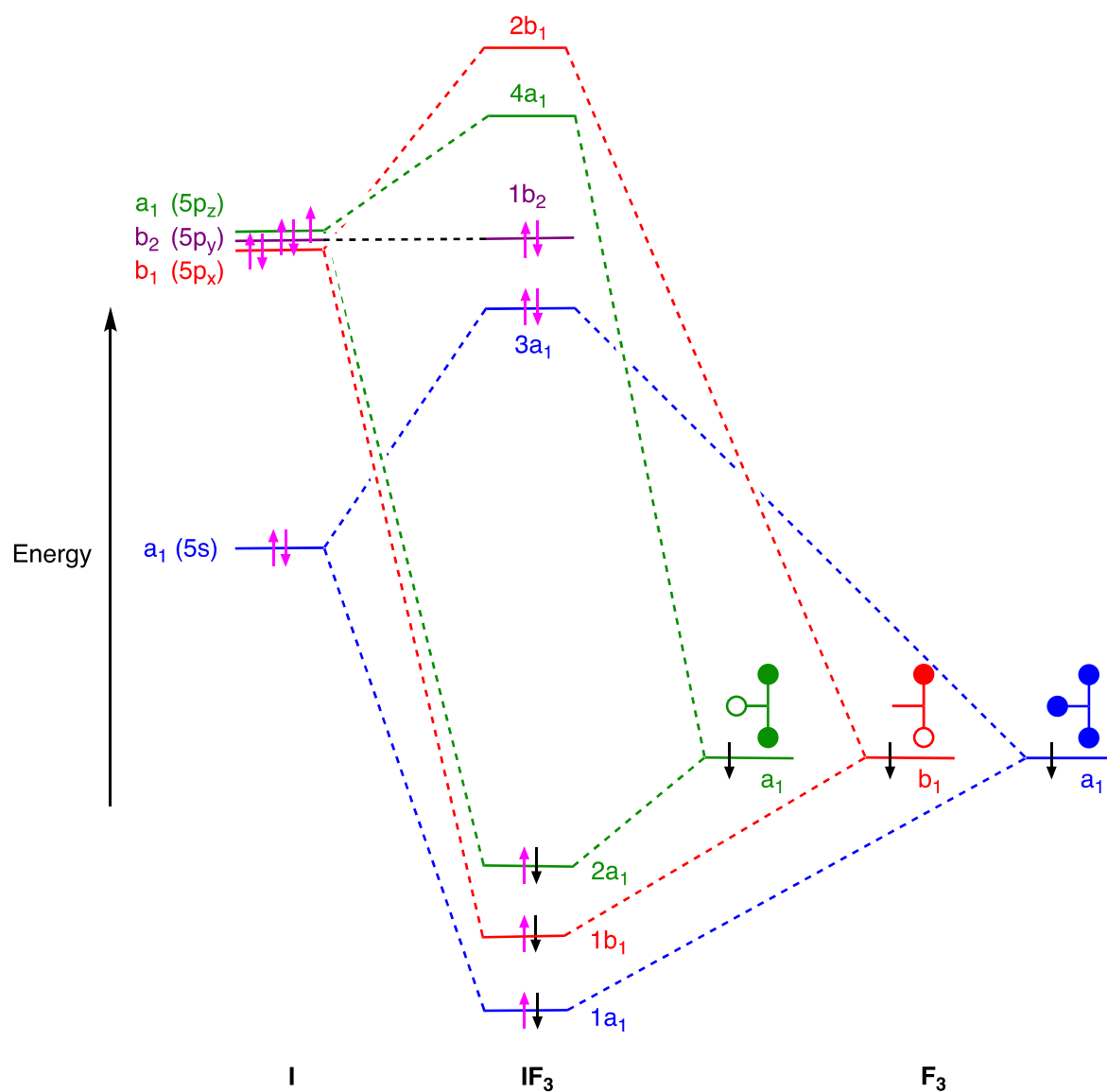


Figure S2 MO diagram for IF_3 showing the filling of the energy levels with electrons from iodine (magenta) and the F_3 LGOs (black). The valency of iodine is 3 and it has 2 "lone pairs" with a_1 and b_2 symmetry.

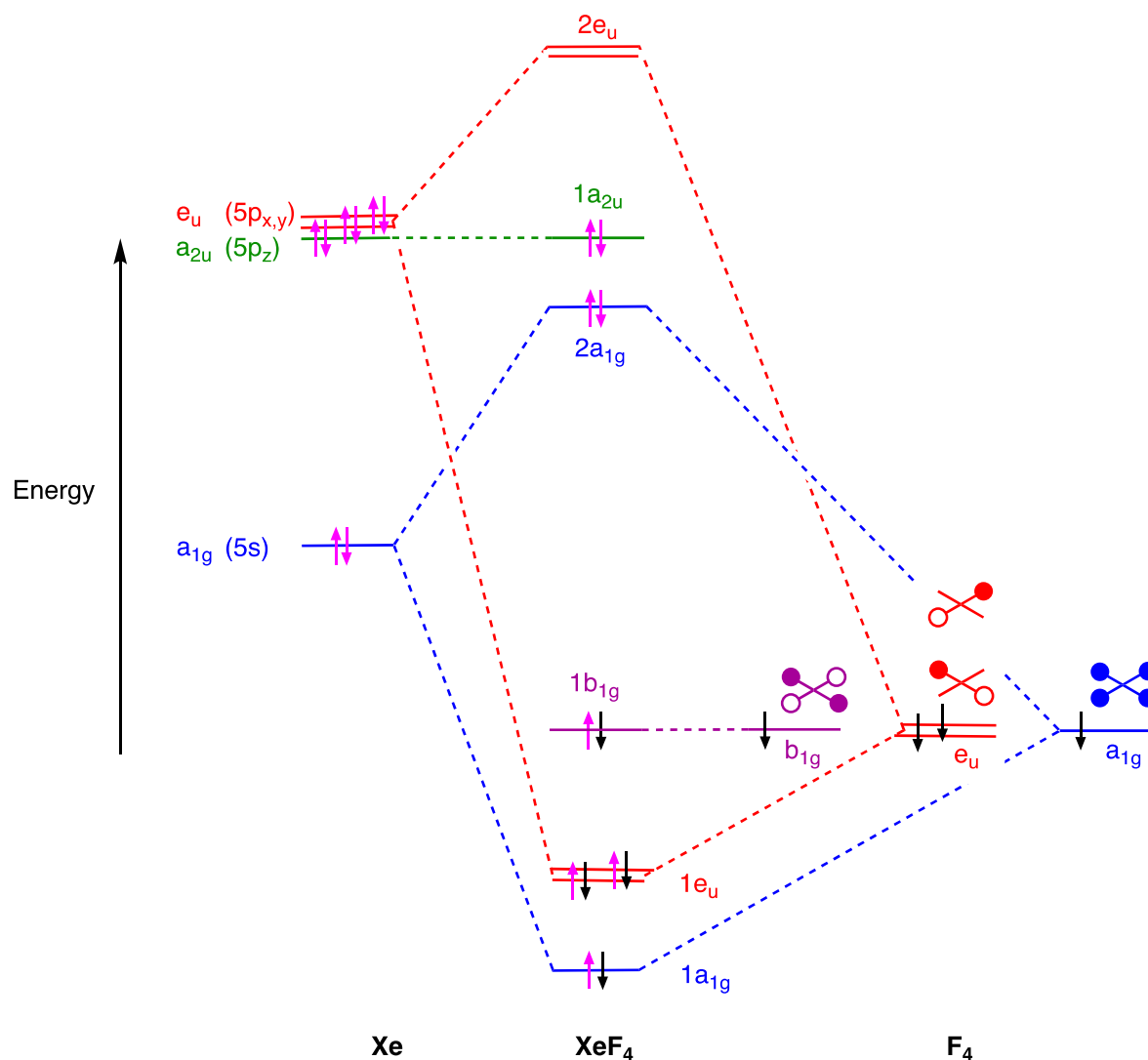


Figure S3 MO diagram for XeF₄ showing the filling of the energy levels with electrons from xenon (magenta) and the F₄ LGOs (black). The valency of xenon is 4 and it has 2 "lone pairs" with a_{1g} and a_{2u} symmetry.

In Section 3, the MO diagrams for the various classes of EX_{*n*} are shown (see pages S8-S20). A similar analysis of these MO diagrams to that given above for IF₃ and XeF₄ leads to an assignment of the lone pairs on E, from which the valence of E can be determined after taking into account any overall charge on the EX_{*n*} species. In each case, the values for the numbers of lone pairs on E and the valence of E (identified in the Notes for each Figure) correlate with the values drawn from the well-known Lewis structures.

2.2 Electron delocalisation on to the F ligands in PF₅ and related species

In the MO energy level diagram for PF₅, the orbital labelled 2a₁' is essentially non-bonding with respect to P–F and is delocalised over all 5 F atoms. The representation shown in Figure S4 indicates that phosphorus is pentavalent and one of the valence electrons on P is delocalised on to the 5 F atoms. This MO picture is similar to the ionic representation **D** of PF₅ (see Figure S4) proposed by Pauling as [PF₄]⁺ F[−] in which the counteranion could be any one the 5 F atoms, i.e., there are 5 resonance canonical forms of **D** (see discussion in Section 3 of the main article).

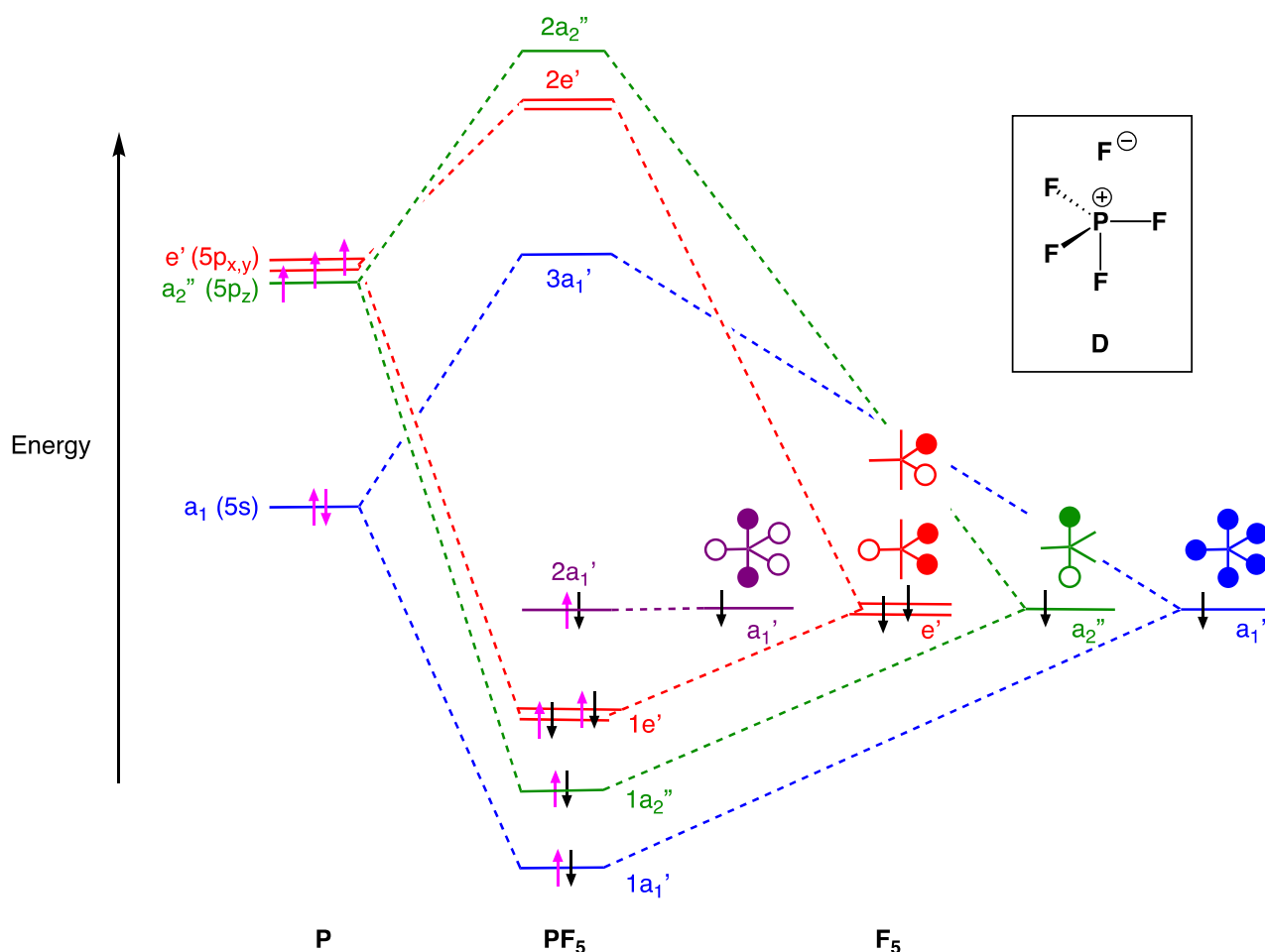


Figure S4. MO diagram for PF₅ showing the filling of the energy levels with electrons from phosphorus (magenta) and the F₅ LGOs (black). The phosphorus is pentavalent and one of its valence electrons is in the 2a₁' MO which is largely localised on the F₅ ensemble. The inset shows a proposed ionic formulation for PF₅.

A similar picture can be envisaged for SF₆ where two of the sulfur valence electrons are located in the 1e_g MO which is delocalised on to the 6 F atoms; this is reminiscent of an ionic structure for SF₆ of the

form $[\text{SF}_4]^{2+} 2\text{F}^-$ which would have multiple resonance canonical forms (see J. M. Galbraith, *J. Chem. Ed.*, 2007, **84**, 783-787). Indeed, any MO picture given in the following Section for an EX_n species that contains electrons in non-bonding orbitals that are localised on X, is amenable to this ionic analysis.

From the MO diagram for $[\text{TeF}_6]^{2-}$ given on page S18, it is not immediately clear how to assign a valency to Te. However, if it is assumed that the electrons from the 2- charge are delocalised on the electronegative F atoms by occupying the $1e_g$ MO (see Figure S5), then the valency of Te is then readily assigned as 4.

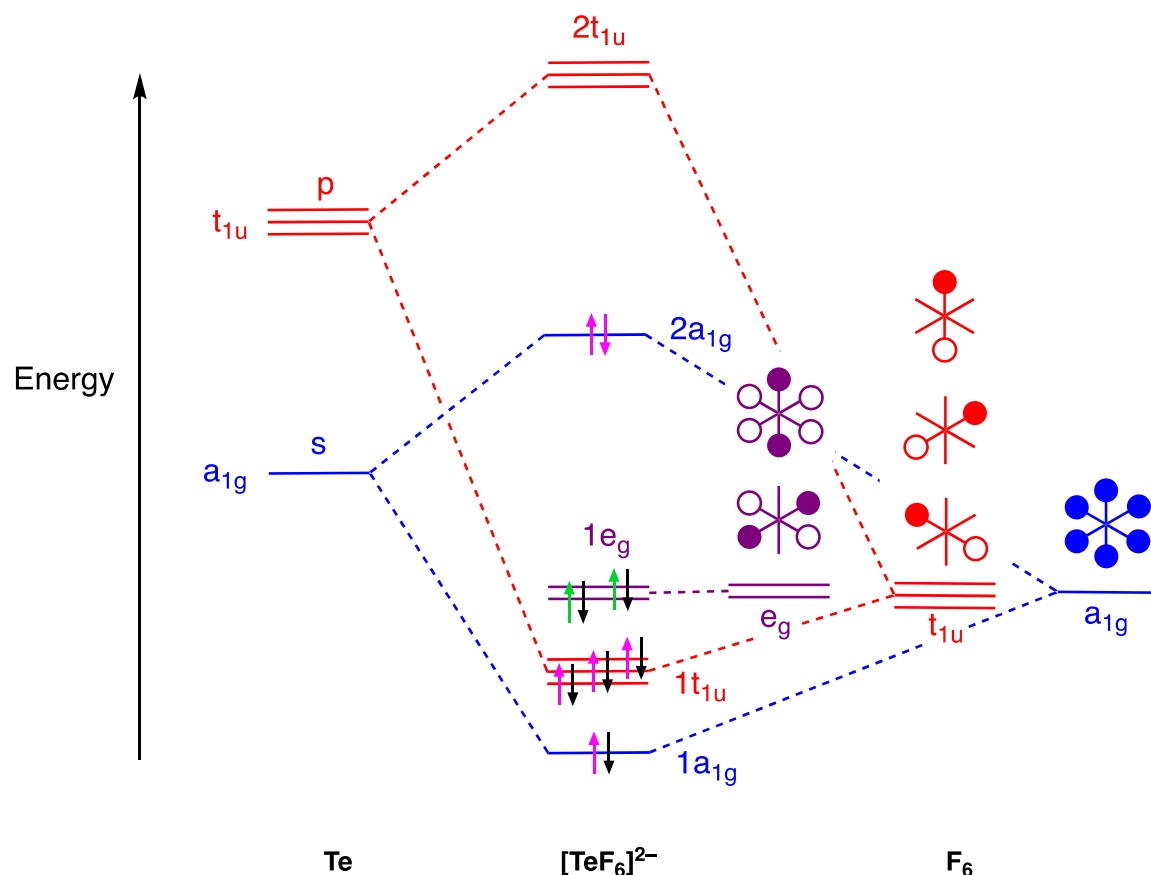


Figure S5 MO diagram for $[\text{TeF}_6]^{2-}$ showing the filling of the energy levels with electrons from tellurium (magenta), the F_6 LGOs (black) and the dianionic charge (green). The valency of tellurium is 4 and it has 1 "lone pairs" with a_{1g} symmetry.

Similar rationales can be given for other anions such as $[\text{SiF}_6]^{2-}$ (silicon valence 4), $[\text{IF}_8]^-$ (iodine valence 7), $[\text{XeF}_8]^{2-}$ (xenon valence 6).

3. General MO energy level diagrams for p-block compounds EX_n

The MO plots in the following pages are categorised according to the electron count and EX_nL_m where *m* is the number of lone pairs L. The colour coding in the Chart below is for the classification of Types I-III compounds given in Figure S1 (page S3). The examples given in the Chart are almost exclusively fluorides although X can, in principle, be any monovalent group with an electronegativity greater than E. In red letters are neutral examples of the particular EX_nL_m configuration and the black-lettered examples are charged species that are isoelectronic with the neutral example.

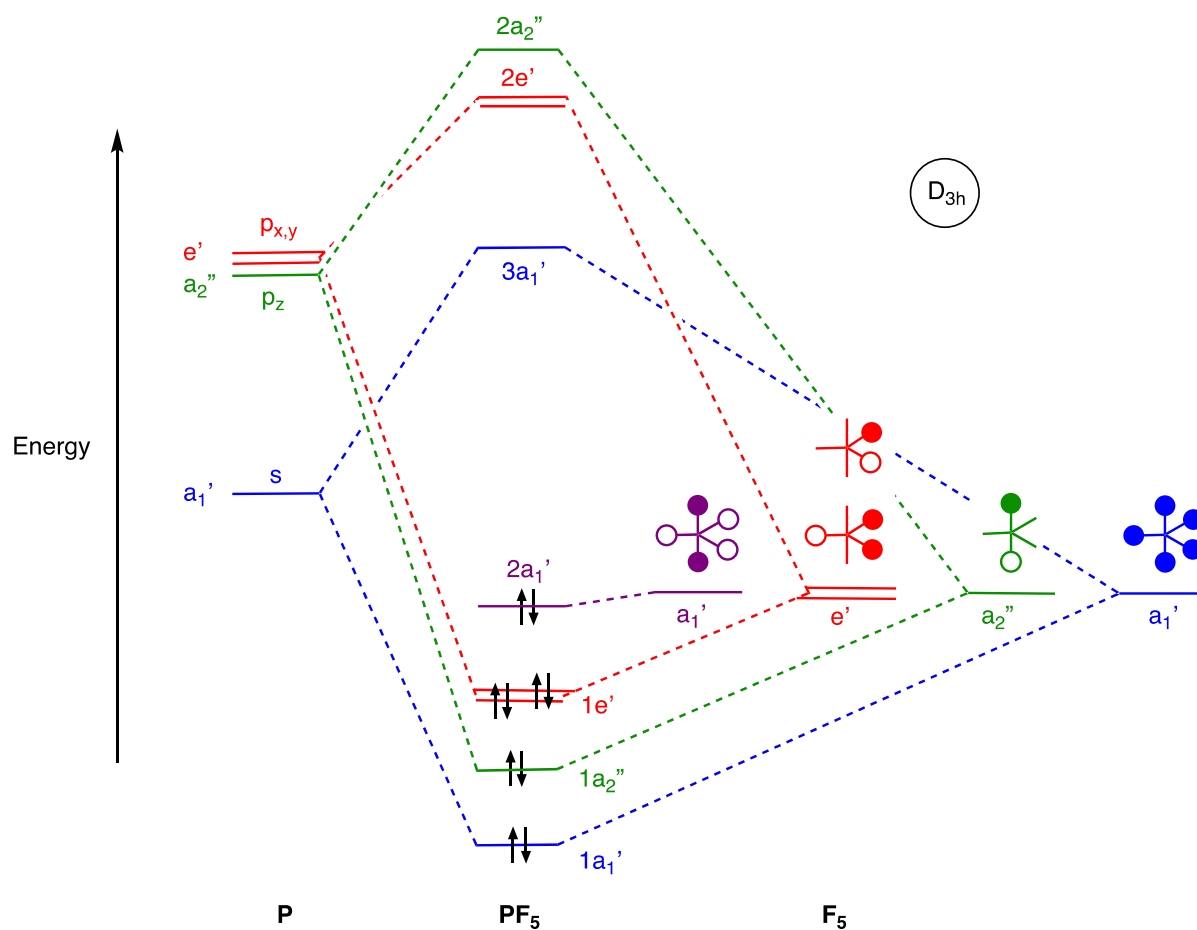
Maximum Group Valence	4	5	6	7	8		Electron Count ^a
	EX ₄ SiF ₄	EX ₃ L PF ₃	EX ₂ L ₂ SF ₂	EXL ₃ IF	EL ₄ Xe		8
		EX ₅ PF ₅ [SiF ₅] ⁻ [AlF ₅] ²⁻	EX ₄ L SF ₄ [PF ₄] ⁻	EX ₃ L ₂ IF ₃	EX ₂ L ₃ XeF ₂ [IF ₂] ⁻ [I ₃] ⁻		10
			EX ₆ SF ₆ [PF ₆] ⁻ [SiF ₆] ²⁻ [AlF ₆] ³⁻ [IF ₆] ⁺	EX ₅ L IF ₅ [TeF ₅] ⁻	EX ₄ L ₂ XeF ₄ [IF ₄] ⁻		12
				EX ₇ IF ₇ [TeF ₇] ⁻	EX ₆ L XeF ₆ [IF ₆] ⁻ [TeF ₆] ²⁻ [SbF ₆] ³⁻		14
					EX ₈ XeF ₈ [IF ₈] ⁻		16
						EX ₈ L [XeF ₈] ²⁻	18

- a This is the valence electron count for the central element, E, obtained from the total number of valence electrons for E plus 1 for each of the X atoms and taking account of the charge: electrons are added for a negative charge and subtracted for a positive charge.

3.1 Ten-electron systems: EX₅, EX₄L, EX₃L₂, EX₂L₃

3.1.1 EX₅ (D_{3h})

An example of this configuration is PF₅ and this is a Type I compound (see Fig. S1).

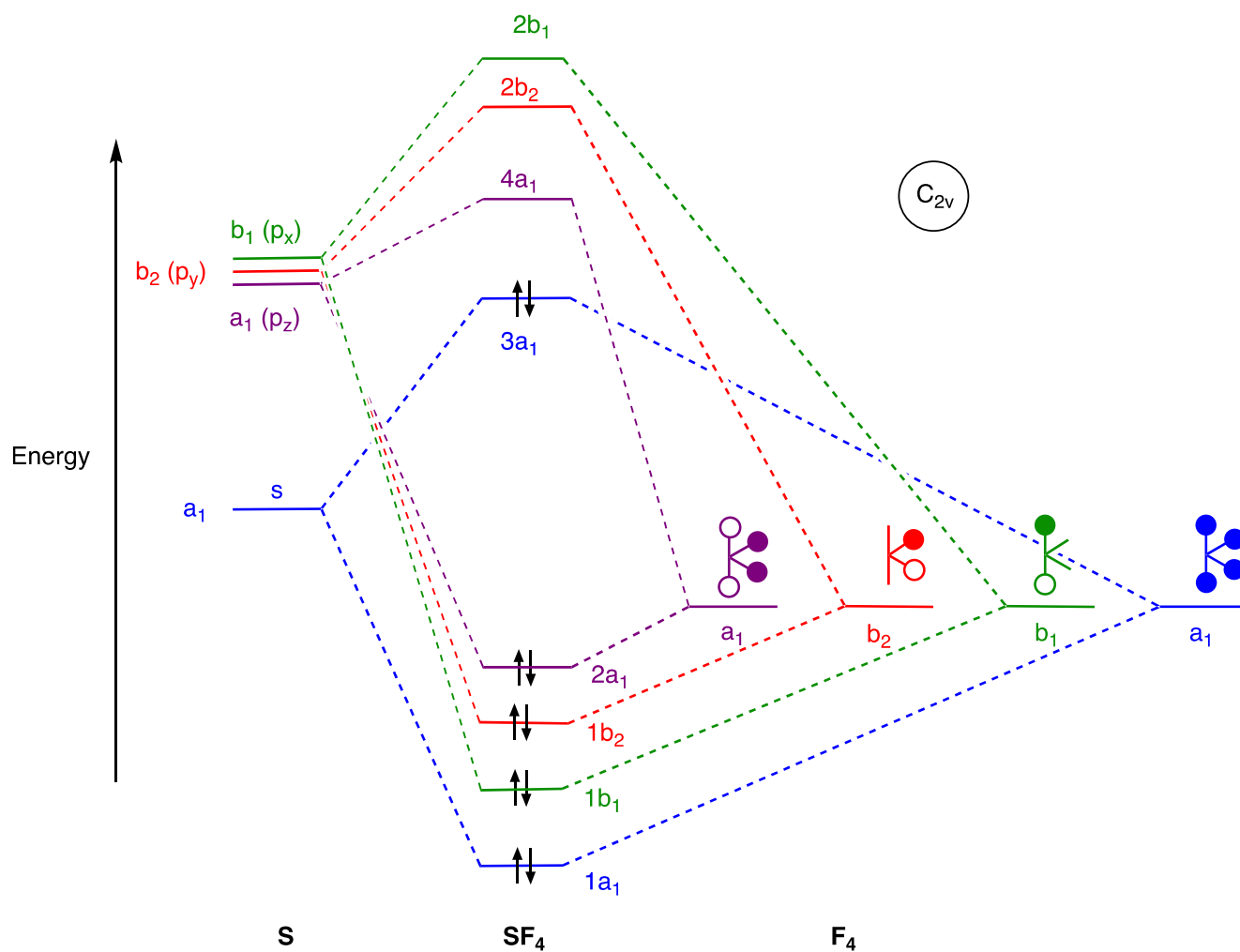


Notes

- The combination of $1a_2''$ and $2a_1'$ is equivalent to a localised 3c,4e interaction.
- The non-bonding $2a_1'$ is delocalised over the 5 F atoms.
- P is pentavalent.

3.1.2 EX₄L (C_{2v})

An example of this configuration is SF₄ and this is a Type II compound (see Fig. S1).

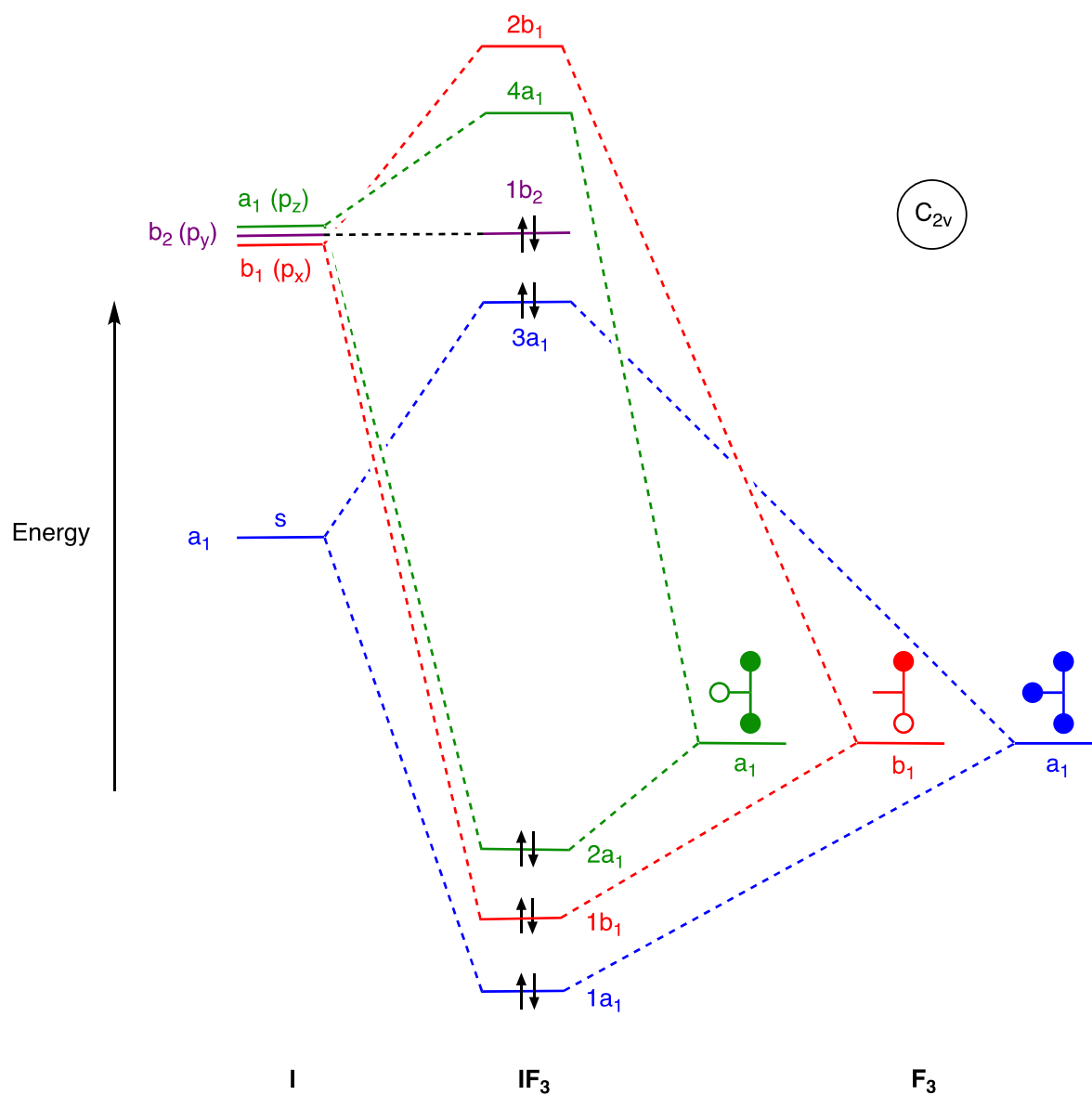


Notes

- If the $3a_1$ orbital is considered to be a lone pair, then this diagram is compatible with the traditional Lewis structure of SF₄ with 4 S–F bonds and a lone pair.
- S is tetravalent.

3.1.3 EX_3L_2 (C_{2v})

An example of this configuration is IF_3 and this is a Type III compound (see Fig. S1).

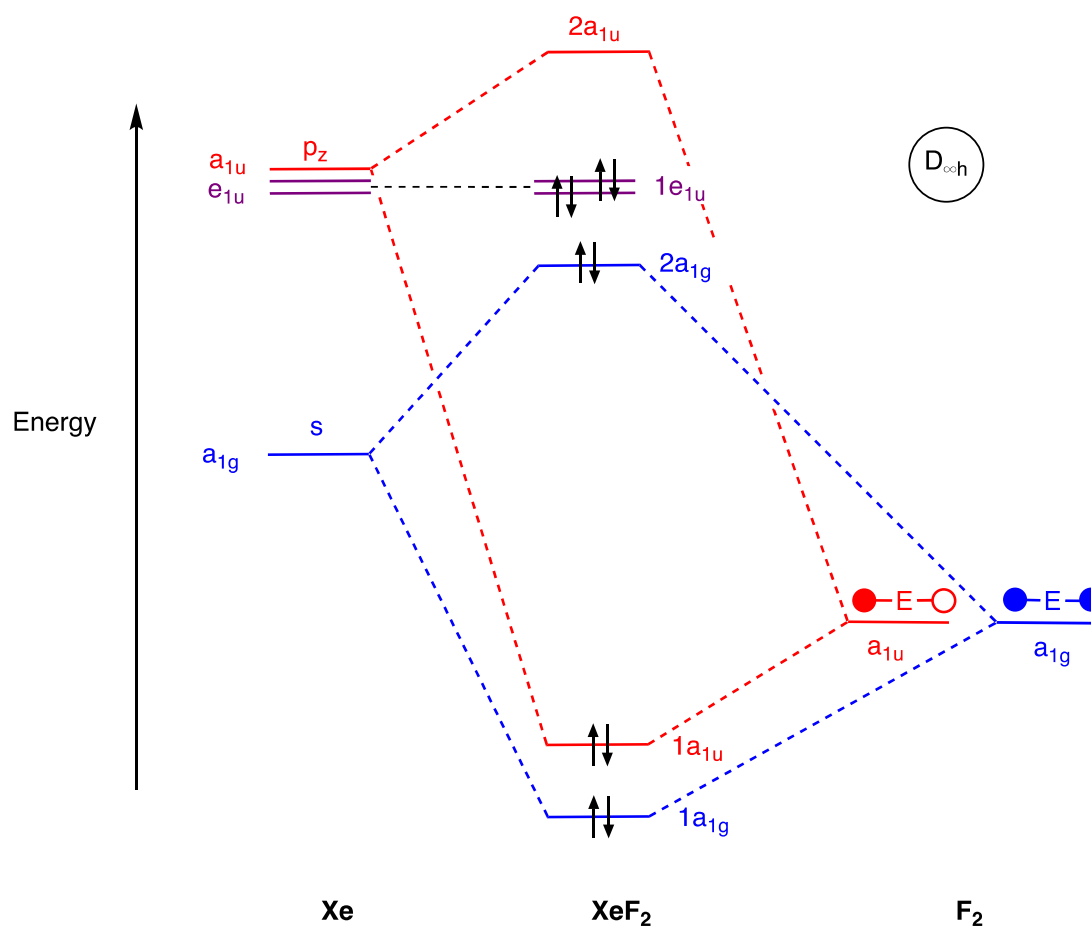


Notes

- If the $3a_1$ and $1b_2$ orbitals are considered to be lone pairs, then this diagram is compatible with the traditional Lewis structure of IF_3 with 3 I–F bonds and 2 lone pairs.
- I is trivalent.

3.1.4 EX_2L_3 ($\text{D}_{\infty\text{h}}$)

An example of this configuration is XeF_2 and this is a Type III compound (see Fig. S1).



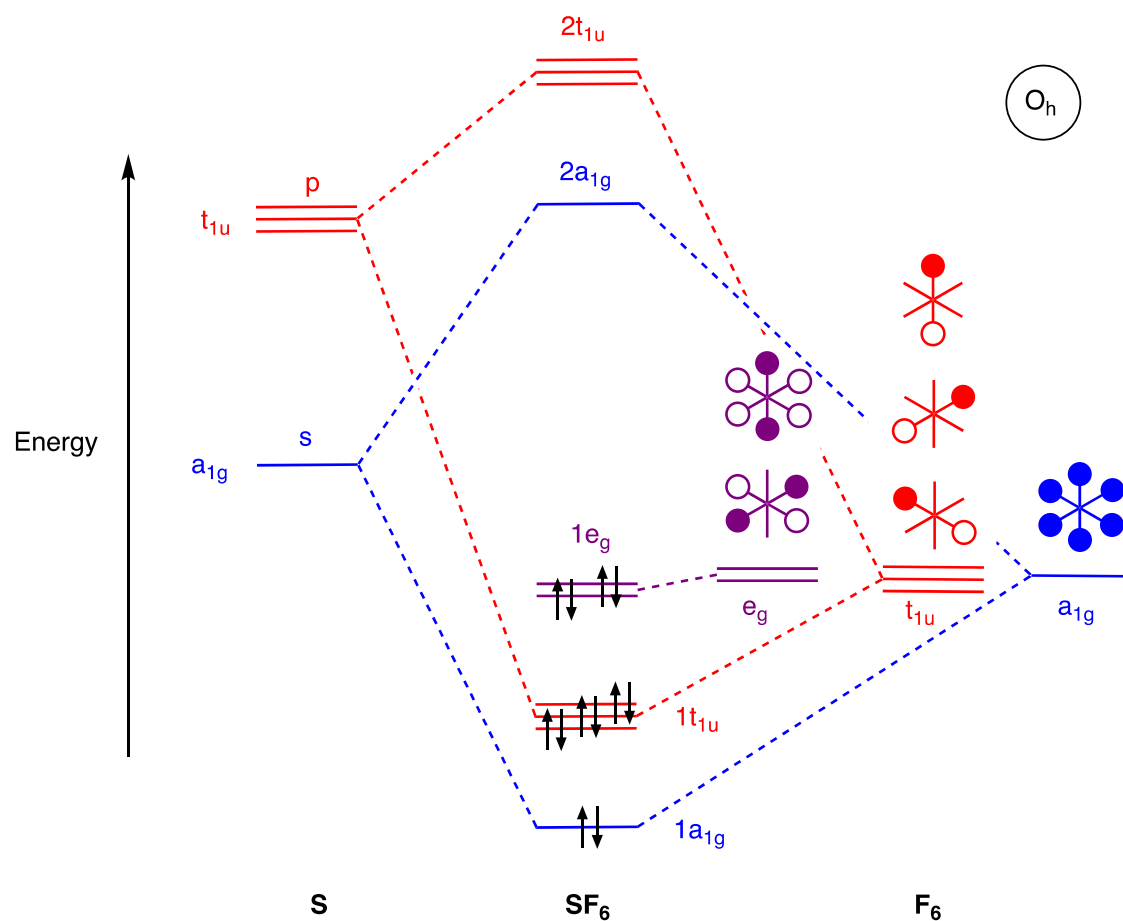
Notes

- If the $2a_{1g}$ and $1e_{2u}$ orbitals are considered to be lone pairs, then this diagram is compatible with the traditional Lewis structure of XeF_2 with 2 Xe–F bonds and 3 lone pairs.
- Xe is divalent.

3.2 Twelve-electron systems: EX_6 , EX_5L , EX_4L_2 , EX_2L_3

3.2.1 $\text{EX}_6 (\text{O}_h)$

An example of this configuration is SF_6 and this is a Type I compound (see Fig. S1).

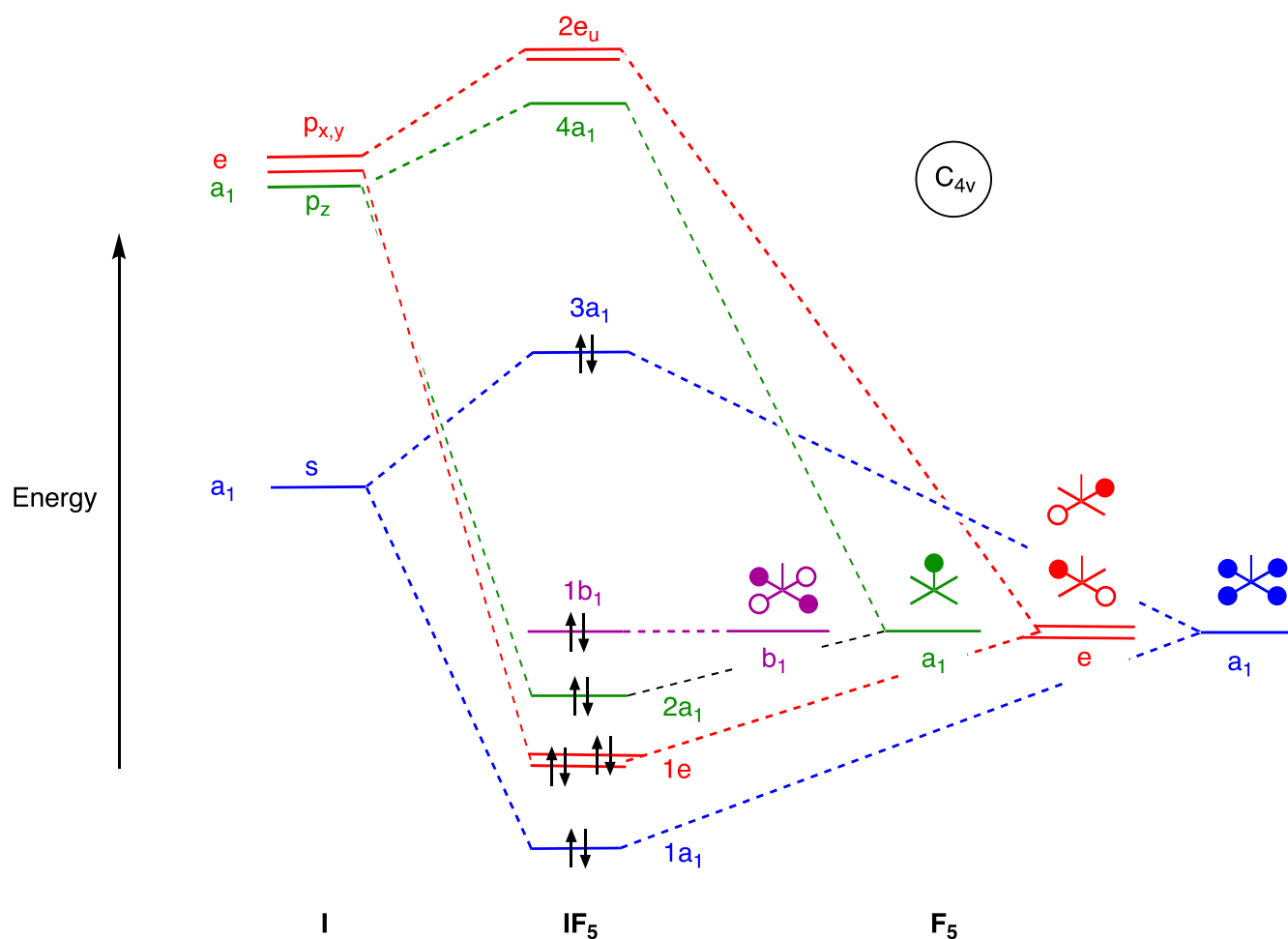


Notes

- The non-bonding $1e_g$ is delocalised over the 6 F atoms.
- S is hexavalent.

3.2.2 EX₅L (C_{4v})

An example of this configuration is IF₅ and this is a Type II compound (see Fig. S1).

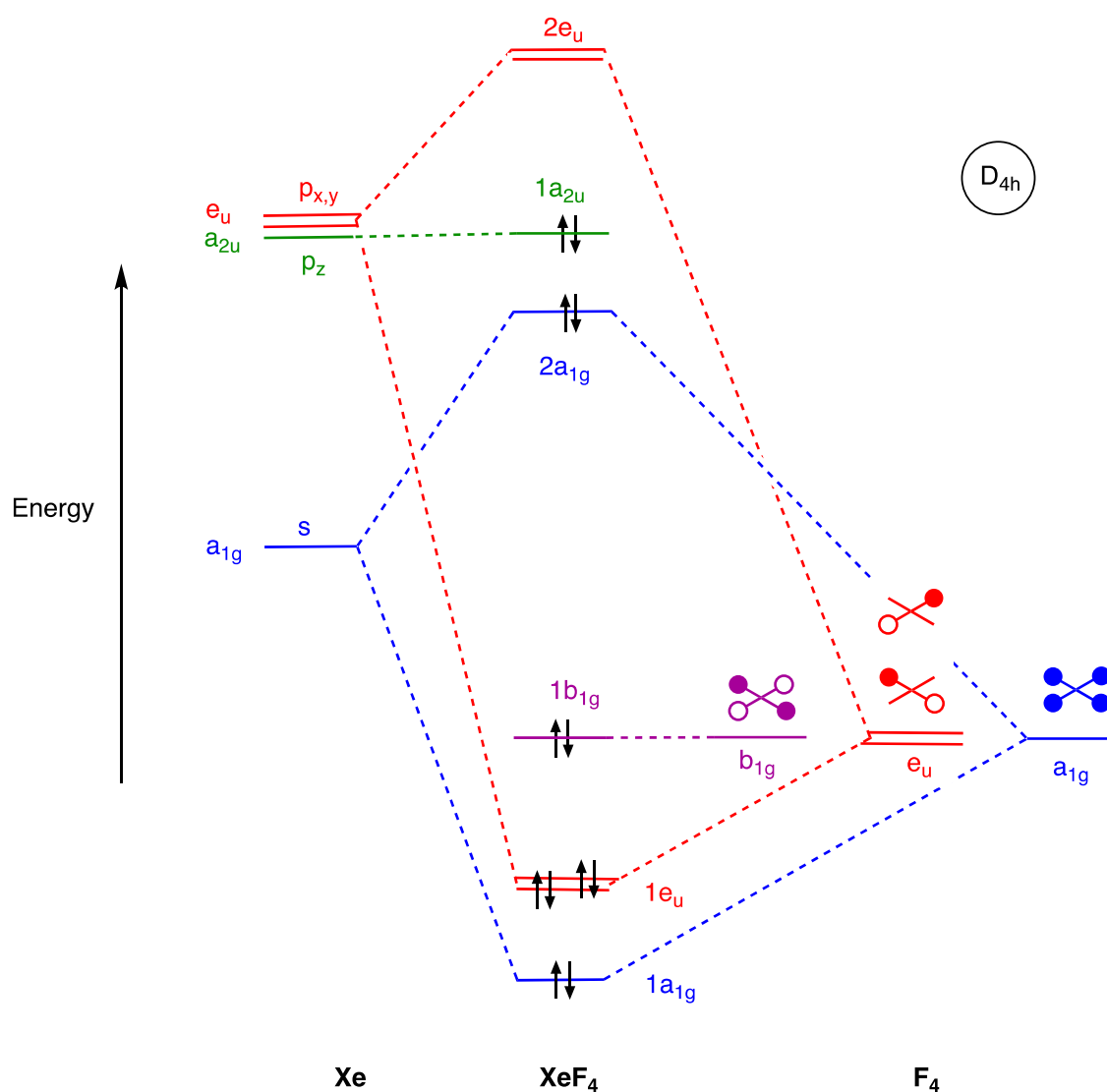


Notes

- If the 3a₁ orbital is considered to be a lone pair, then this diagram is compatible with the traditional Lewis structure of IF₅ having 5 I–F bonds and 1 lone pair.
- The non-bonding 1b₁ is delocalised over the 4 basal F atoms.
- I is pentavalent.

3.2.3 EX₄L₂ (D_{4h})

An example of this configuration is XeF₄ and this is a Type III compound (see Fig. S1).



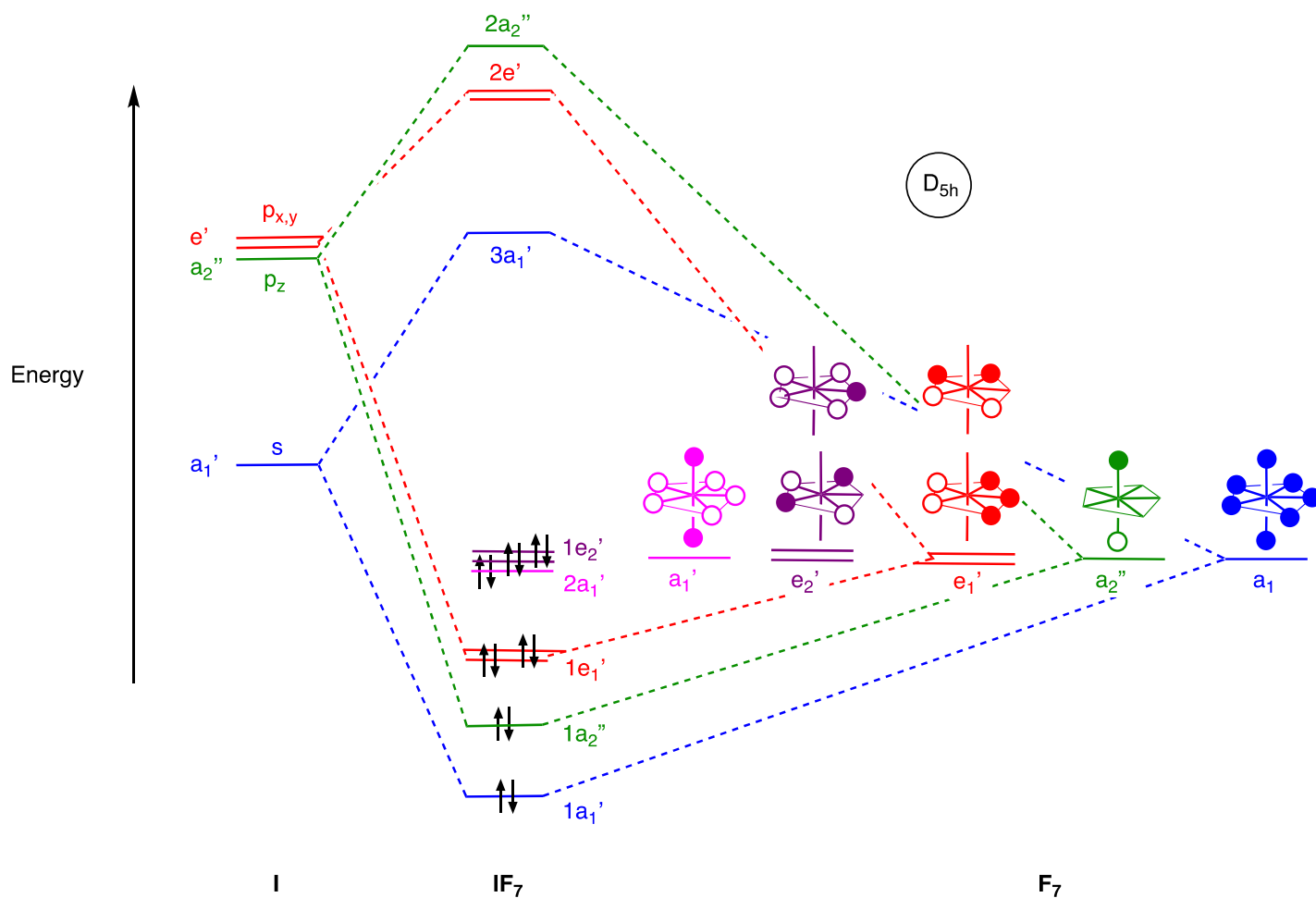
Notes

- If the 2a_{1g} and 1a_{2u} orbitals are considered to be lone pairs, then this diagram is compatible with the traditional Lewis structure of XeF₄ with 4 Xe–F bonds and 2 lone pairs.
- The non-bonding 1b_{1g} is delocalised over the 4 F atoms.
- Xe is tetravalent.

3.3 Fourteen-electron systems: EX₇, EX₆L,

3.3.1 EX₇ (D_{5h})

An example of this configuration is IF₇ and this is a Type I compound (see Fig. S1).

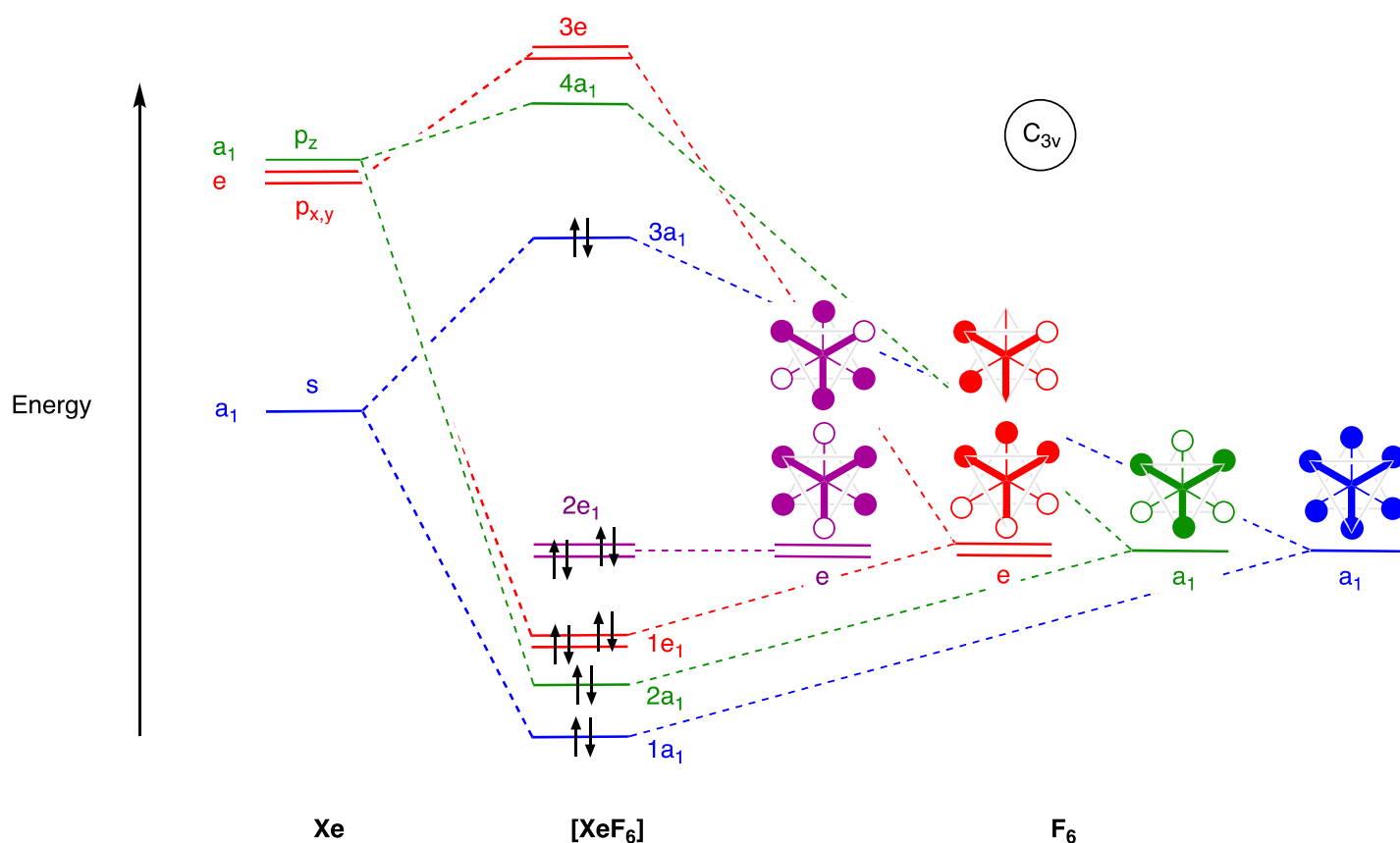


Notes

- The 2a₁' is delocalised over all 7 F atoms and the e₂' is delocalised over the 5 equatorial F atoms.
- I is heptavalent.

3.3.2 EX₆L (C_{3v})

An example of this configuration is XeF₆ and this is a Type II compound (see Fig. S1).

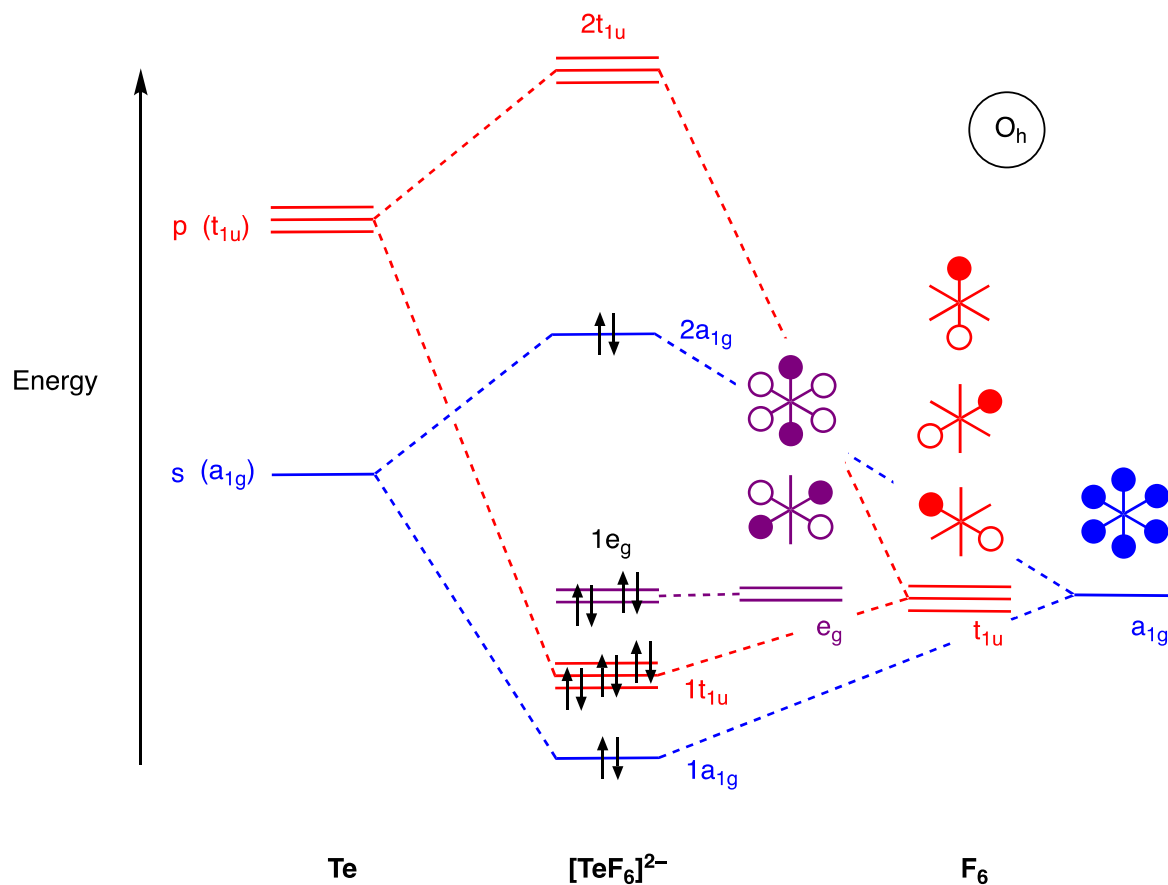


Notes

- If the 3a₁ orbital is considered to be a lone pair, then this diagram is compatible with the traditional Lewis structure of XeF₆ having 1 lone pair.
- Calculations show that this face-capped octahedral (C_{3v}) structure is the lowest energy structure, but two other geometries (C_{2v} and O_h) are very close in energy.
- The non-bonded 2e₁ is delocalised over the 6 F atoms.
- Xe is hexavalent.

3.3.3 EX₆L (O_h)

An example of this configuration is [TeF₆]²⁻ and this is a Type II species (see Fig. S1).

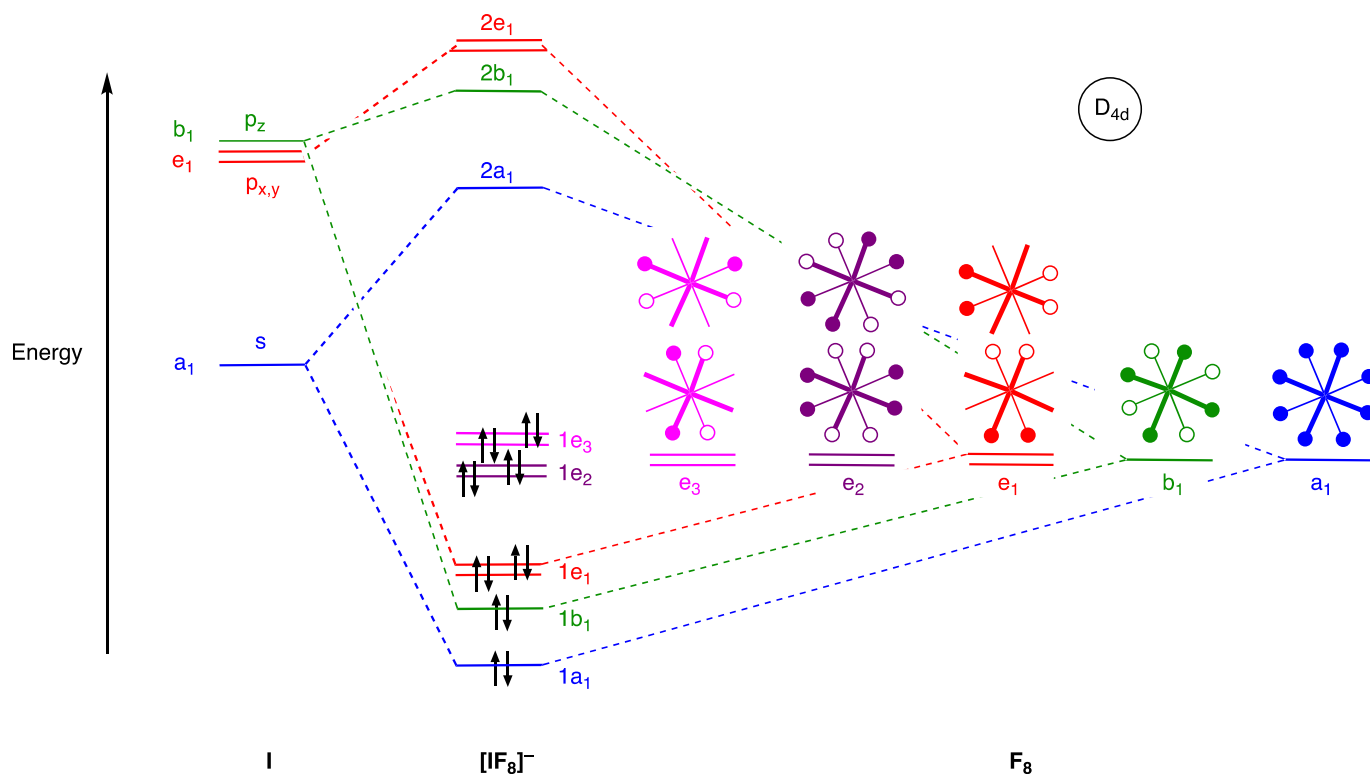


Notes

- The non-bonded 1e_g is delocalised over the 6 F atoms.
- If the 2a_{1g} orbital is considered to be a lone pair on Te, of the 12e in the lower energy levels, 6e are contributed by the 6F and 2e are associated with the 2- charge therefore this diagram is compatible with Te being tetravalent.

3.4 Sixteen-electron systems: EX₈ (D_{4d})

An example of this configuration is [IF₈][−] and this is a Type I species (see Fig. S1).

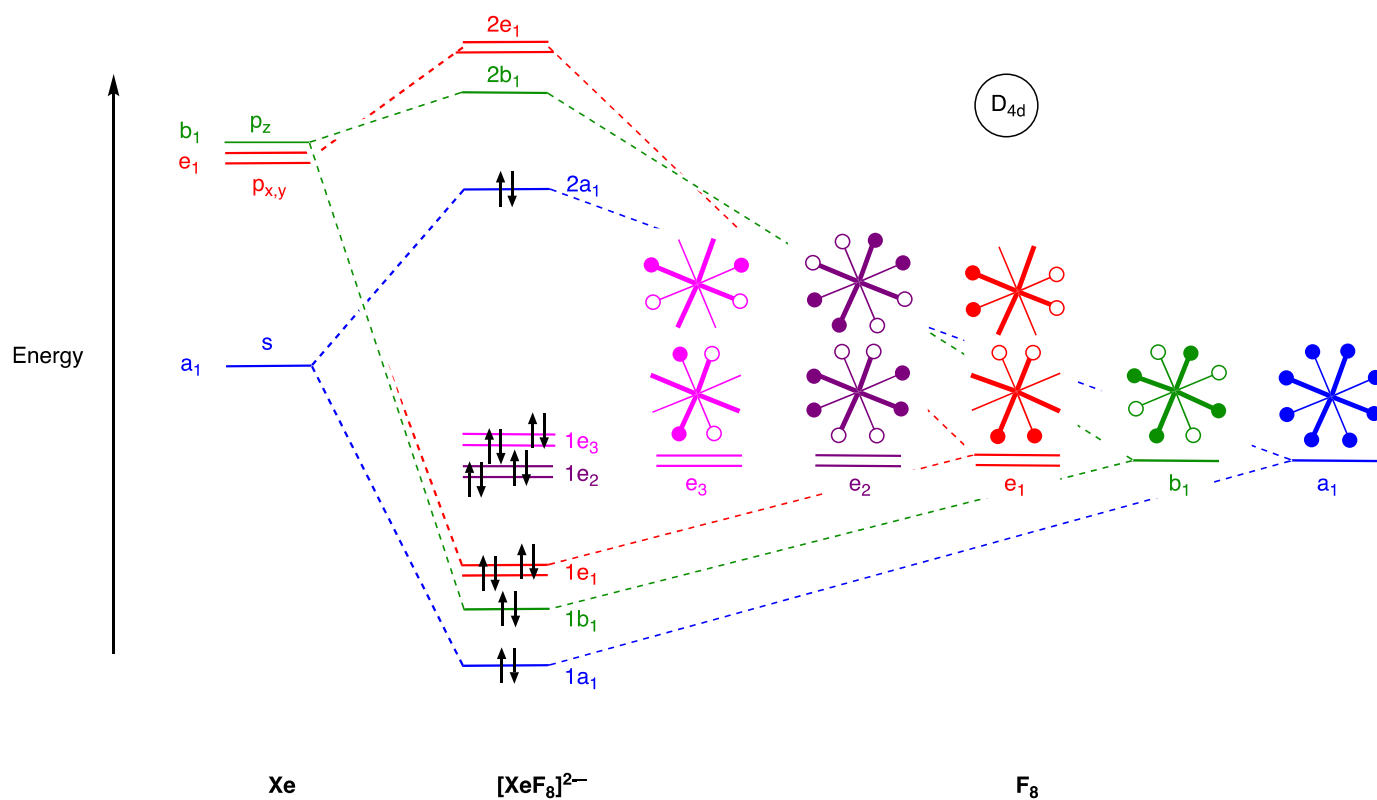


Notes

- The neutral compound XeF₈ is unknown but calculations indicate that it would have the same D_{4d} structure as above.
- The non-bonding 1e₂ and 1e₃ are delocalised over the 8 F atoms
- Of the 16e, 8e are contributed by the 8F and 1e is associated with the 1− charge, and so the I is heptavalent.

3.5 Eighteen-electron systems: EX₈L (D_{4d})

The only example of this configuration is [XeF₈]²⁻ and this is a Type II species (see Fig. S1).



Notes

- This 18e dianion has no possible neutral analogue.
- The non-bonding 1e₂ and 1e₃ are delocalised over the 8 F atoms.
- If the 2a₁ orbital is considered to be a lone pair on Xe, of the 16e in the lower energy MOs, 8e are contributed by the 8F and 2e are associated with the 2- charge, and hence the Xe is hexavalent.