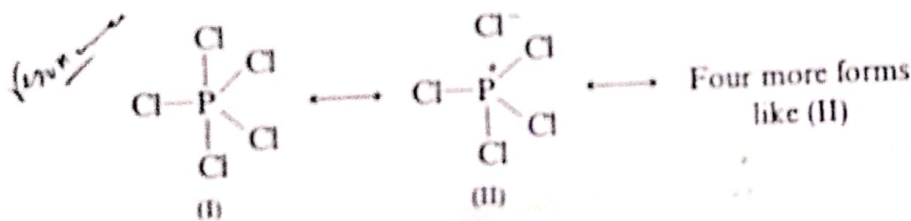


Fig. 17.5 The 3*d* orbital distribution functions in *d*<sup>1</sup> configurations: (A) in the <sup>6</sup>*D* term of P(*sp*<sup>3</sup>*d*); (B) in the <sup>5</sup>*D* term of S(*s*<sup>2</sup>*p*<sup>3</sup>*d*). Line represents a typical S—F bond length. [Modified from K. A. R. Mitchell, *Chem. Rev.*, 1969, 69, 157. Reproduced with permission.]

electrons and hence do not feel the nuclear charge as much as the 3*s* and 3*p* electrons. As a result they are extremely diffuse, having radial distribution maxima at a distance which is approximately twice a typical bond distance (Fig. 17.5). This results in extremely poor overlap and weak bonding.<sup>18</sup>

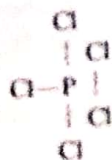
Two alternatives have been provided to account for the higher oxidation states of the nonmetals without invoking the use of the high energy *d* orbitals. Pauling has suggested that resonance of the following type could take place.<sup>19</sup>



Only structure I involves *d* orbitals, and so the *d* character of the total hybrid is small. Each P—Cl bond has 20% ionic character and 80% covalent character from resonance structures such as II. Pauling has termed the “extra” bonds formed (over and above the

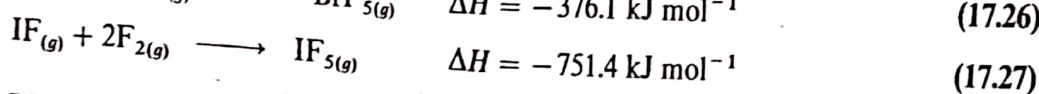
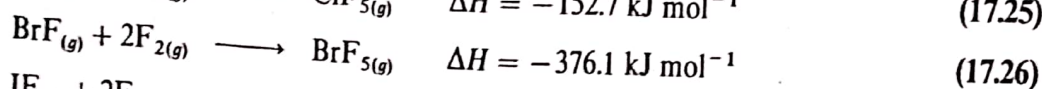
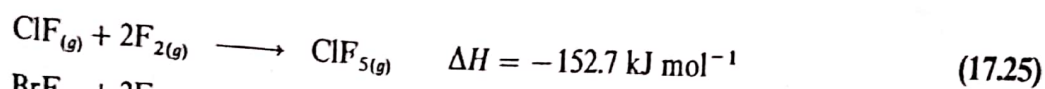
<sup>18</sup> A point that may easily be overlooked in this regard is that the poor overlap results not only from the poor spatial arrangement of a diffuse orbital but also from the concomitant low value of the wave function,  $\Psi$ , at any particular point in space, and so a low buildup of electron density from  $\Psi_1 \cdot \Psi_2$ .

<sup>19</sup> Pauling listed a third type of canonical structure,



but pointed out that the Cl—Cl interaction is a very “long bond” and does little to stabilize the molecule. [L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp. 177–179.]

four in a noble gas octet or "argononic" structure) as "transargononic" bonds and pointed out that they tend to be weaker than "normal" or "argononic" bonds and form only with the most electronegative ligands. Thus the average bond energy in  $\text{PCl}_3$  is  $317 \text{ kJ mol}^{-1}$  but in  $\text{PCl}_5$  it is only  $165 \text{ kJ mol}^{-1}$ .<sup>20</sup> The same effect is found in  $\text{PF}_3$  and  $\text{PF}_5$ , but in this case the difference in bond energy is only  $61.1 \text{ kJ mol}^{-1}$ , corresponding to the stabilization of the structure by increased importance of the ionic structures in the fluorides. The stabilization of these structures by differences in electronegativity is exemplified by the tendency to form the higher halogen fluorides.<sup>21</sup> The enthalpies of fluorination of the halogen monofluorides are:



The second alternative is the three-center, four-electron bond developed by simple molecular orbital theory for the noble gas fluorides (see pp. 767-769). Since this predicts that each bonding pair of electrons (each "bond") is spread over three nuclei, the bond between two of the nuclei is less than that of a normal two-center, two-electron bond. Furthermore, since the nonbonding pair of electrons is localized on the fluorine atoms, there is a separation of charge ("ionic character"). In both respects, then, this interpretation agrees with Pauling's approach and with the experimental facts.

#### Theoretical arguments in favor of *d* orbital participation

In contrast to the arguments presented against participation by *d* orbitals in the bonding of nonmetals, several workers have pointed out that the large promotion energies and diffuse character described above are *properties of an isolated sulfur atom*. What we need to know are the *properties of a sulfur atom in a molecule*, such as  $\text{SF}_6$ . This is an exceedingly difficult problem and cannot be dealt with in detail here.<sup>22</sup> However, we have seen how it is possible to calculate such properties as electronegativity on isolated atoms as charge is added or withdrawn (see pp. 153-155) and how this might *approximate* such properties in a molecular environment.

It is apparent from the preceding discussions that participation of *d* orbitals, if it occurs at all, is found only in the nonmetals when in high oxidation states with electronegative substituents. The partial charge induced on the central P or S atom will be large merely from the electronegativity of the fluorine (as in  $\text{PF}_5$ ,  $\text{SF}_6$ ) or oxygen (as in  $\text{OPX}_3$ ,  $\text{O}_2\text{SX}_2$ ) irrespective of any bonding model (such as Pauling's or the three-center bond) invoked.

<sup>20</sup> For a more complete discussion of this point, see L. Pauling, "General Chemistry," 3rd ed., Freeman, San Francisco, 1970, pp. 244-247.

<sup>21</sup> See Table 15.2 and attendant discussion. The values in Eqs. 17.25-17.27 differ slightly from those given by Pauling (footnote 20) in order to be self-consistent with the values in Table 15.2.

<sup>22</sup> For a detailed discussion of this complex problem, see K. A. R. Mitchell, *Chem. Rev.*, 1969, 69, 157, and references therein.



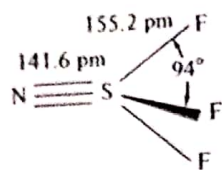


Fig. 17.6 Molecular structure of thiazyl trifluoride,  $\text{NSF}_3$ .

We have seen in Chapter 2 that the  $3d$  orbital lies above the  $4s$  orbital at atomic number 20 but falls below as the atomic number increases. Furthermore, in the  $M^{+2}$  ions the  $3d$  orbital lies below the  $4s$  orbital at least as soon as atomic number 22 ( $\text{Ti}^{+2}$  is  $d^2$ , not  $s^2$ ). This is a general phenomenon: Increasing effective nuclear charge makes the energy levels of an atom approach more closely the degenerate levels of the hydrogen atom. We might expect, in general, that increasing the effective nuclear charge on the central atom as a result of inductive effects would result in the lowering of the  $d$  orbitals and hence will be more sensitive to changes in electron density. The promotion energy would thus be lowered. A second effect of large partial charges on the central atom will be a shrinking of the large, diffuse  $d$  orbitals into smaller, more compact orbitals that will be more effective in overlapping neighboring atomic orbitals. For example, sample calculations indicate that in  $\text{SF}_6$  the  $d$  orbitals have been contracted to an extent that the radius of maximum probability is only 130 pm compared with the large values in the free sulfur atom.

#### Experimental evidence for $d$ orbital contraction and participation

One of the most remarkable molecules is thiazyl trifluoride,  $\text{NSF}_3$  (Fig. 17.6). This compound is very stable. It does not react with ammonia at room temperature, with hydrogen chloride even when heated, or with metallic sodium at temperatures below  $400^\circ\text{C}$ . The S—N bond, 141.6 pm, is the shortest known between these two elements. The FSF bond angles of  $94^\circ$  are compatible with approximate  $sp^3$  bonding<sup>23</sup> and the presence of an  $sp^3$  hybrid  $\sigma$  bond and two  $p-d$   $\pi$  bonds between the sulfur and the nitrogen. The contraction of the  $d$  orbitals by the inductive effect of the fluorine atoms presumably permits effective overlap and  $\pi$ -bond formation. The alternative explanation would require a double dative bond from the sulfur atom, extremely unlikely in view of the positive character of the sulfur atom.

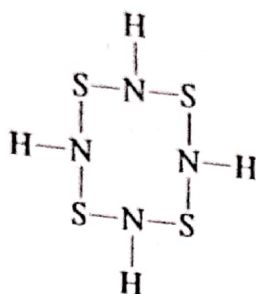
The bond length is consistent with a triple bond. Bond lengths of 174 pm for single S—N bonds (in  $\text{NH}_2\text{SO}_3\text{H}$ ) and 154 pm for double S=N bonds (in  $\text{N}_4\text{S}_4\text{F}_4$ ) are consistent with a bond order of 2.7 in thiazyl trifluoride. This value is also in agreement with an estimate based upon the force constant.<sup>24</sup> The relative bond lengths of S—N, S=N,

<sup>23</sup> Some  $d$  orbital hybridization may enter into the  $\sigma$  system, reducing the bond angles.

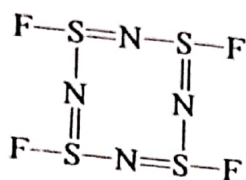
<sup>24</sup> Of course, this involves certain assumptions about the relation between the force constant and bond order. For a more complete discussion of bond length and bond order in these compounds, see O. Glemser and M. Fild, *Halogen Chem.*, 1967, 2, 1. See also O. Glemser and R. Mews, *Adv. Inorg. Radiochem.*, 1970, 14, 33.

and  $S \equiv N$  bonds are thus 1.00:0.88:0.81 compared with similar shortenings of 1.00:0.87:0.78 for corresponding  $C-N$ ,  $C=N$ , and  $C \equiv N$  bonds.

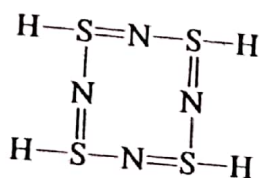
Two other molecules indicating the influence of fluorine substitution on  $d$  orbital participation are  $S_4N_4H_4$  and  $N_4S_4F_4$  (see pp. 716–718). Tetrasulfur tetraimide is isoelectronic with the  $S_8$  molecule and so the structure:



and corresponding crown conformation appear quite reasonable. The fluoride, however, has an isomeric structure with substitution on the sulfur atoms:



Double bonding in this molecule is clearly shown by the alternation in  $S-N$  bond lengths in the ring (see Fig. 14.21b). Now both the above electronic structure for  $S_4N_4F_4$  and that for  $S_4N_4H_4$  are reasonable but raise the question: Why doesn't tetrasulfur tetraimide isomerize from the  $N$ -substituted form to the  $S$ -substituted form isoelectronic with the fluoride:



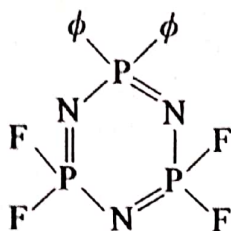
retaining the same number of  $\sigma$  bonds and gaining four  $\pi$  bonds? Apparently the reason the isomerism does not take place is that although  $\pi$  bonding is feasible in the presence of the electronegative fluorine atoms, it is so weak with electropositive hydrogen substituents that it cannot compensate for the weakening of the  $\sigma$  bonding as the hydrogen atom shifts from the more electronegative nitrogen atom to the less electronegative sulfur atom.<sup>25</sup>

Presumably substitution by halogens in the phosphonitrilic series results in contracted  $d$  orbitals and more efficient  $\pi$  bonding in the ring. It was noted previously (see

<sup>25</sup> This argument is based on the stabilization of the  $H-X$   $\sigma$  bonds by ionic resonance energy and is supported by the bond energies in  $NH_3$  ( $391 \text{ kJ mol}^{-1}$ ) and  $H_2S$  ( $347 \text{ kJ mol}^{-1}$ ).



p. 708) that unsymmetrical substitution may allow the normally planar trimeric ring to bend. A good example of this is found in 1,1-diphenylphosphonitrilic fluoride trimer.<sup>26</sup>



3, 3, 5, 5 Tetrafluoro  
triphenylphosphazene

The three nitrogen atoms and the fluoro-substituted phosphorus atoms are coplanar (within 2.5 pm), but the phenyl-substituted phosphorus atom lies 20.5 pm above this plane. The explanation offered is that the more electropositive phenyl groups cause an expansion of the phosphorus *d* orbitals, less efficient overlap with the *p* orbitals of the nitrogen atom, and a weakening of the  $\pi$  system at that point. This allows<sup>27</sup> the ring to deform and the  $\phi_2\text{P}$  moiety to bend out of the plane.

A further example of the jeopardy involved in casually dismissing *d* orbital participation is the findings of Haddon and co-workers<sup>28</sup> that *d*-orbital participation is especially important in  $\text{S}_4\text{F}_4$ , which is nonplanar, and also that it accounts for about one-half of the delocalization energy in the one-dimensional conductor  $(\text{SN})_x$ . In the latter case, the low electronegativity of the *d* orbitals (see p. 181) increases the ionicity of the S—N bond and stabilizes the structure.

Finally, it will be recalled that the existence of strong  $\text{P}=\text{O}$  bonds in  $\text{OPF}_3$  (see p. 828) is consistent with enhanced back donation of electron density from the oxygen atom to the phosphorus atom bearing a positive partial charge from the four  $\sigma$  bonds to electronegative atoms. In light of the above discussion of the contraction of phosphorus and sulfur *d* orbitals when bearing a positive charge, better overlap may be added to the previous discussion as a second factor stabilizing this molecule.

The question of *d* orbital participation in nonmetals is still an open controversy. In the case of  $\sigma$ -bonded species such as  $\text{SF}_6$  the question is not of too much importance since all of the models predict an octahedral molecule with very polar bonds. Participation in  $\pi$  bonding is of considerably more interest, however. Inorganic chemists of a more theoretical bent tend to be somewhat skeptical, feeling that the arguments regarding promotion energies and poor overlap have not been adequately solved. On the other hand, chemists interested in synthesis and characterization tend to favor the use of *d* orbitals in describing these compounds, pointing to the great heuristic value that has been provided by such descriptions in the past and feeling that until rigorous *ab initio* calculations<sup>29</sup> on these molecules show the absence of significant *d* orbital participation it is too soon to abandon a useful model.

<sup>26</sup> C. W. Allen et al., *J. Am. Chem. Soc.*, 1967, 89, 6361.

<sup>27</sup> Note that this explanation provides a rationale which allows the bending but does not provide a driving force to make the ring bend; however, if the ring is sufficiently weakened, small perturbing forces such as those of crystal packing might be sufficient to deform the ring even though the same forces would have little effect in an unweakened ring system.

<sup>28</sup> R. C. Haddon et al., *J. Am. Chem. Soc.*, 1980, 102, 6687.

<sup>29</sup> Not likely in the near future.