Ab Initio Calculations of the Bonding in Krypton Difluoride

By G. A. D. COLLINS, D. W. J. CRUICKSHANK,* and A. BREEZE
(*Chemistry Department, UMIST, Manchester* M60 1QD)

Summary *Ab initio* molecular-orbital calculations show that krypton 4*d* orbitals must be included to give an adequate description of the bonding; addition of 5*s* and 5*p* orbitals does not affect this conclusion.

ALL-ELECTRON SCFMO calculations have been carried out on KrF_2 in order to further understanding of the bonding in rare-gas compounds. The molecule was assumed linear with a Kr–F length of 1·9 Å.[1] (A later measurement gives 1·875 or 1·867 Å.[2]) The calculations were performed with the ATMOL group of programs.[3] The basis orbitals consisted of a set of Slater-type orbitals, each orbital being represented by three Gaussian-type functions, with coefficients and exponents taken from Stewart.[4]

Three calculations have been made on this 54-electron molecule: the first with a minimum basis set with best-atom exponents;[5] the second with the addition of Kr 4*d* Slater functions with exponent 1·3; and the third with the further addition of Kr 5*s* and 5*p* Slater functions each with exponent 1·625. This value was chosen so as to give radial probability maxima in the same region as for the 4*d* orbitals ($r_{\max} = 1 \cdot 63$ Å). The results are summarised in the Table, where column M refers to the minimum basis set, MD to the set with 4*d* functions, and MDSP to the set with 5*s* and 5*p* functions added.

Addition of the 4*d* functions causes a considerable lowering in total energy (0·306 a.u. = 8·3 ev), and has important effects on the overlap population and on three molecular orbitals. In the minimum-basis representation there is very little Kr–F overlap population (covalent bond-order), whereas with the 4*d* functions the overlap population rises to 0·419 electrons.

The top occupied orbital $8\pi_g$ is chiefly the σ_g component of the fluorine lone-pairs. In the M set it is slightly antibonding between Kr and F, and has main components

$$0\cdot 25\ \mathrm{Kr}(4s) + 0\cdot 71\ [\mathrm{F}(2p_z) - \mathrm{F}'(2p_z)].$$

In the MD set it becomes a slightly bonding orbital

$$0\cdot 26\ \mathrm{Kr}(4s) - 0\cdot 23\ \mathrm{Kr}(4d_{z^2}) + 0\cdot 11\ [\mathrm{F}(2s) + \mathrm{F}'(2s)] + 0\cdot 67[\mathrm{F}(2p_z) - \mathrm{F}'(2p_z)],$$

and its orbital energy drops by 0·162 a.u. = 4·4 ev.

By symmetry, the non-bonding $4\pi_u$ orbitals have no possible 4*d* component, whereas the $2\pi_g$ orbitals have no possible Kr *s* or *p* components. Introduction of Kr(4*d*)

Results for KrF_2

	M	MD	MDSP
		Total energy (a.u.)	
	−2921·536	−2921·842	−2921·922
		Energies of outer orbitals (a.u.)	
$8\sigma_g$	−0·155	−0·317	−0·351
$4\pi_u$	−0·341	−0·419	−0·448
$2\pi_g$	−0·363	−0·500	−0·525
$3\pi_u$	−0·566	−0·599	−0·627
$5\sigma_u$	−0·574	−0·643	−0·672
$7\sigma_g$	−1·104	−1·141	−1·169
$4\sigma_u$	−1·351	−1·460	−1·488
$6\sigma_g$	−1·374	−1·475	−1·503
		Atomic populations	
Total Kr	35·365	35·845	35·967
Total F	9·318	9·078	9·017
Total 4*d*		0·697	0·682
$4d\pi$		0·486	0·482
		Overlap population for each Kr–F	
Total	0·045	0·419	0·505
$p\pi - p\pi$	−0·014	−0·014	0·033
$d\pi - p\pi$		0·235	0·234
$d\sigma - F\sigma$		0·079	0·079
		Quadrupole moments (a.u.)	
$Q_{xx} = Q_{yy}$	−17·15	−18·86	−19·58
Q_{zz}	−24·61	−22·67	−22·53

changes the $2\pi_g$ pair of orbitals from non-bonding to bonding with main components of type,

$$0{\cdot}25\,\mathrm{Kr}(4d_{xz}) + 0{\cdot}64\,[\mathrm{F}(2p_x) - \mathrm{F}'(2p_x)],$$

and the orbital energy falls by 0·137 a.u. = 3·7 ev.

When the 5*s* and 5*p* functions are added the picture does not change greatly. The total energy drops by a further 2·2 ev, and the $5p_x$ and $5p_y$ orbitals each acquire populations of 0·142 electrons. (The 5*s* and $5p_z$ have only 0·053 and 0·016 electrons.) The extra flexibility in the basis set allows more charge around Kr near the *xy* plane, as indicated by the increased Q_{xx} and Q_{yy} electric quadrupole moments.

In the M basis the Mulliken gross charge on Kr is +0·64; in the extended bases it is much reduced. The effect is not just a simple consequence of the introduction of diffuse Kr orbitals which can interpenetrate the fluorine regions, since the quadrupole moment difference $Q_{zz} - Q_{xx}$ is more than halved on extension of the basis.

The 4*d* populations are practically the same in the MD and MDSP bases, and it is evident that 4*d* orbitals are essential for an adequate description of the bonding in KrF_2.

We thank Drs. Hillier and Saunders for the use of the ATMOL program, and the S.R.C. for a research grant.

(*Received, June 8th,* 1970; *Com.* 881.)

---

[1] H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, 1965, **42**, 1229.

[2] C. Murchison, S. Reichman, D. Anderson, J. Overend, and F. Schreiner, *J. Amer. Chem. Soc.*, 1968, **90**, 5690.

[3] I. H. Hillier and V. R. Saunders, *Chem. Phys. Letters*, 1969, **4**, 163.

[4] R. F. Stewart, *J. Chem. Phys.*, 1970, **52**, 431.

[5] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686.