The Molecular Orbital Energy Levels and Bonding in Krypton Difluoride

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Summary The valence level photoelectron spectrum of KrF_2 indicates an identical M O ordering to that of XeF_2 and a remarkable similarity of orbital energies

THE ionization potentials of gaseous KrF_2 up to 30 ev, measured by high-resolution (25 mv) molecular photo-electron spectroscopy using He (I) (21 2 ev) and He (II)

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(40 8 ev) photon sources and a 127° electrostatic energy analyser are given in the Table The orbital assignments are

Ionization potentials and orbital assignments for KrF_2

Vertical I P (ev)	Orbital Assignment
13 34 ⎱ 13 47 ⎰	$4\pi_u$
13 90	$8\sigma_g$
14 37	$2\pi_g$
16 92	$3\pi_u$
17 7	$5\sigma_u$
23 0[a]	$7\sigma_g$

[a] He II recorded only

made on the basis of the observation of spin–orbit splitting and a comparison to the by now well-established levels in XeF_2[1,2] The first I P , consisting of the spin–orbit doublet $^2\pi_{3/2}$ and $^2\pi_{\frac{1}{2}}$ at 13 34 ev and 13 47 ev, relates to removal of a $4\pi_u$ electron.   The second I P exhibits no spin–orbit splitting as it relates to the removal of a σ-electron $(8\sigma_g)$

Recently a set of three *ab initio* M O calculations were reported,[3] (a) with a minimum basis set, (b) with the addition of Kr $4d$ orbital functions and, (c) with the further addition of Kr $5s$ and $5p$ functions On the basis of a lowering in total energy and some changes in overlap population it was concluded that $4d$ participation was necessary for an adequate bonding description of KrF_2 The $4\pi_u$ and $8\sigma_g$ energies for calculation (b) were *ca* 11 4 ev and 8 6 ev, respectively substantially different from the experimental I P 's The remaining levels are more in agreement with experiment (Figure) Calculation (a) is in even poorer agreement with experiment, yielding an extremely low first orbital energy $(8\sigma_g)$ of 4 3 ev and a second energy of 9 2 ev A calculation elsewhere on XeF_2,[1,4] using a much higher quality basis set, provided agreement with the experimental I P's without inclusion of d orbitals [i e equivalent to (a)] We would suggest for KrF_2 that the lack of agreement with experiment indicates that the existing *ab initio* calculations are not of sufficiently high accuracy to say whether or not $4d$ orbitals are important in the bonding

It has been demonstrated for other molecules[5,6] that d orbital functions can sometimes appear very prominent in
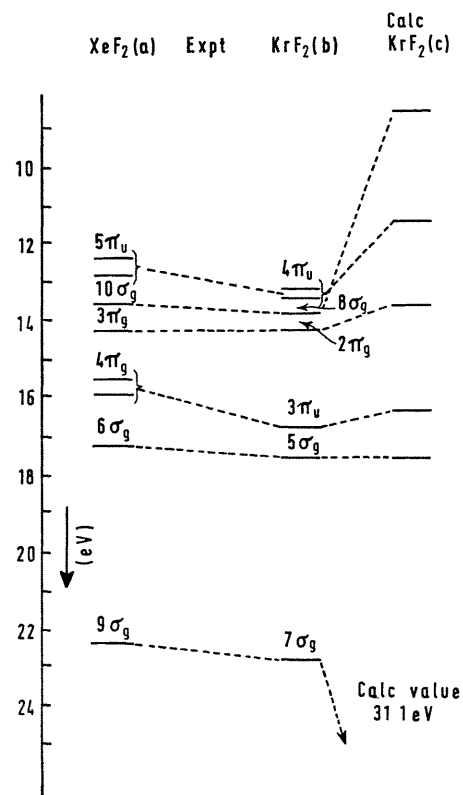

FIGURE   *Energy level diagram for* XeF_2 *and* KrF_2 (a) *Ref* 1, (b) *present results*, (c) *ref* 3

calculations at a low quality basis set level, but when the quality of the other basis functions is improved the need to include d functions is reduced

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