

The Influence of d Orbitals on the Shape of Monomeric CaF₂

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Extensive *ab initio* calculations have shown that d orbitals on Ca are responsible for the non-linearity of monomeric CaF₂ and that a surprisingly large d basis on Ca is necessary.

The shape of monomeric CaF₂ has been an intriguing puzzle for over 25 years, to which Beattie and co-workers have recently drawn attention.¹ Three standard, usually reliable qualitative approaches to molecular structure concur: according to VSEPR theory,² to Walsh's rules³ (CaF₂ has sixteen valence electrons, like CO₂), and on electrostatic grounds (if an ionic formulation is preferred), CaF₂ 'should' be linear. However, gas-phase electric deflection experiments⁴ have shown CaF₂ to be non-linear, and bond angles of 140(3)⁵ or 142(1)⁶ have been reported in IR studies of matrix-isolated CaF₂. Quantitative *ab initio* results have been variable,^{7–10} with both linear^{8,10} and bent^{7,9} shapes predicted, but the variationally best results^{8,10} suggest linearity, in apparent conflict with experiment. We have undertaken a thorough theoretical study of CaF₂, in which we have systematically varied the size of the d basis on Ca. We report that CaF₂ is definitely non-linear at the SCF level, that d orbitals on Ca are responsible for the bending, that the variability in previous results^{7–10} is due to inadequate d bases, and that a surprisingly large Ca d (Gaussian) basis is needed to obtain consistent, converged structural predictions.

The program Gaussian 86¹¹ was used for all *ab initio* calculations. A flexible 8s7p Ca basis was derived from Wachters' 14s9p primitives,¹² supplemented by a diffuse p set (exponent 0.12). For fluorine we used a triple-zeta (10,6)/[5,3] basis,¹³ augmented by a set of diffuse p functions (exponent 0.07). A series of calculations was performed, in which the

structure of CaF₂ was optimized, and the bending force constant determined for a linear geometry. The size of the d basis on Ca was progressively increased through this series. Results for CaF₂ are summarized in Table 1.

In calculations in which the Ca and F bases were restricted to the s,p sets described above, a linear geometry was obtained in which the bending force constant of 0.117 aJ rad⁻² was much smaller than those found in typical rigid molecules such as CO₂ (0.785 aJ rad⁻²).¹⁴ When a single set of d functions (optimum exponent 0.34) was added to Ca, the bending force constant was effectively halved. (It is important to note that the optimum single d exponents for the ³D and ²D states of Ca and Ca⁺ of 0.018 and 0.037 are *much* smaller than for molecular CaF₂; this highlights the danger in choosing d exponents for molecules from atomic calculations). The sensitivity of the force constant to exponent is striking; a value of 0.101 aJ rad⁻² was found with a d exponent of 0.20, which is almost twice that obtained with the optimum exponent. Addition of a set of d functions to F (exponent 1.0) had a modest rather than dramatic effect on the bending force constant, so exponent optimization was not considered necessary in this case.

Multiple exponents for d basis functions on Ca were optimized within the 'even-tempered' convention, where the multiplicative ratio between successive d functions is fixed. In each case both that ratio and the value of the smallest exponent were optimized to the number of significant figures

Table 1. *Ab initio* results for linear CaF₂.

Ca Basis d space	F Basis d space	Ca d exp	Ratio ^a	$r_{\text{Ca-F}}/\text{\AA}$	E^b /hartree	k^c /aJ rad ⁻²
0	0	—	—	2.1258	0.80809	0.1167
1	0	0.34	—	2.0727	0.83260	0.0590
1	1	0.39	—	2.0608	0.84142	0.0455
2	1	0.33	5.4	2.0404	0.85106	0.0226
3	1	0.26	4.2	2.0351	0.85451	0.0092
4	1	0.13	3.9	2.0324	0.85581	-0.0092
5	1	0.13	3.0	2.0323	0.85640	-0.0124

^a Multiplicative ratio between successive d exponents. ^b Energy below -875.0 hartree. ^c Bending force constant.

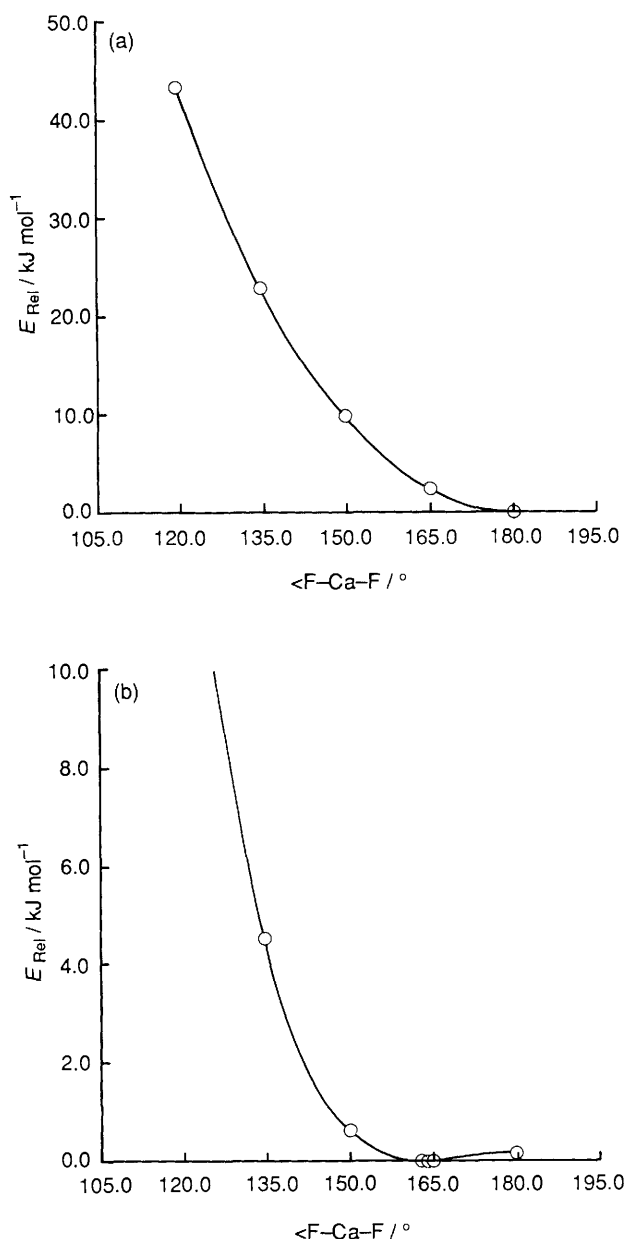


Figure 1. Variation of energy with bond angle for CaF_2 ; (a) no d functions, (b) with d functions in Ca basis.

shown in Table 1. Use of a second set of d functions on Ca led to a further halving of the bending force constant and an energy gain (9.6 mhartree) which was large enough to warrant further expansion of the Ca d basis. There is a steady reduction in the value of the bending force constant as the size of the d basis is enlarged, until CaF_2 becomes non-linear when four sets of d functions are used (note the negative force constant in Table 1). Judging by the predicted properties (Table 1), the Ca d basis is effectively saturated with five sets. The astonishing sensitivity of the bending force constant in CaF_2 to the details of the d basis on Ca explains why such variable results have been obtained in other *ab initio* calculations⁷⁻¹⁰ in which the d basis was chosen with less care than here.

The optimum bond angle for CaF_2 at the SCF level with the 5d Ca basis is 162.9°, and the bond length is 2.0290 Å. In

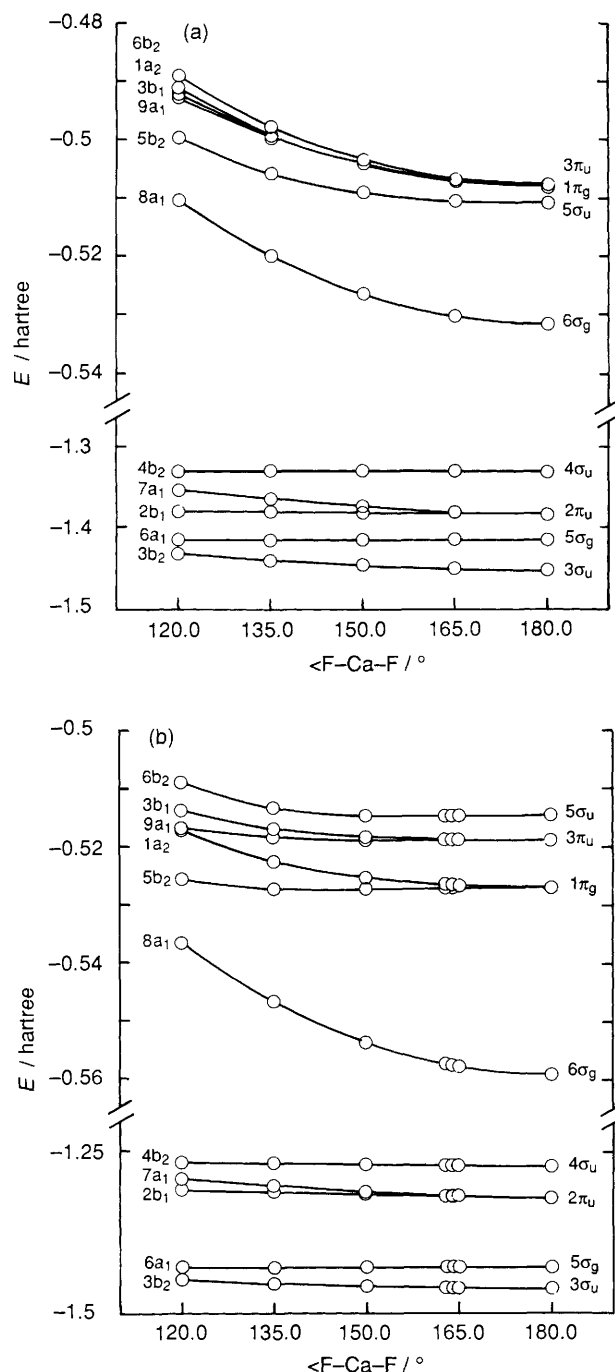


Figure 2. Valence orbital energies for CaF_2 ; (a) no d functions, (b) with d functions in Ca basis.

Figure 1 we display the energy of CaF_2 as a function of bond angle, both excluding [Figure 1(a)] and including [Figure 1(b)] Ca d orbitals. Bending the molecule causes the Ca-F bond to shrink slightly; with the 5d basis, the distances are 2.0323 (180), 2.0298 (165), 2.0229 (150), and 2.0139 Å (135°), but smaller changes are seen if d orbitals are excluded. CaF_2 is a 'quasi-linear' molecule, since its energy of -875.85647 hartree is just 0.18 kJ mol⁻¹ (15 cm⁻¹) below that obtained when linearity is enforced. Since the bending potential shown in Figure 1(b) is strongly anharmonic, calculation of the bending vibrational frequency for CaF_2 using the harmonic approach would not give accurate results. Although our calculated value

of the bond angle does not match the results of 140° ⁵ or 142° ⁶ obtained from vibrational spectroscopy particularly well, there are several reasons why exact agreement might not be expected. (i) Vibrational anharmonicity was necessarily neglected in the experimental bond angle determinations;^{5,6} this procedure is known¹⁵ to give results which are systematically low. (ii) Since the bending potential for CaF_2 is so flat, even weak interactions with the 'inert' matrix may lead to bond angles which are significantly different from those in the gas phase. (iii) The calculations refer to hypothetical molecules with no vibrational energy, whereas even in a matrix at 4 K all molecules have at least the zero-point vibrational energy. As this energy is many times greater than the energy lowering predicted to result from bending CaF_2 from linearity to a bond angle of 162.9° , the equilibrium and effective bond angles may differ. (iv) Although our Ca basis appears to be saturated as far as d functions are concerned, the possible role of higher angular momentum functions cannot be ignored. Addition of a single set of f functions (exponent 0.4) to the optimum three d set produced a reduction in the bending force constant of 40%; although this reduction is small in absolute terms, it suggests that CaF_2 would be more acutely bent if a complete basis were used. The substantial energy lowering caused by this single set of f functions (7.1 mhartree) also shows that higher functions cannot be neglected.

Since CaF_2 is predicted to be bent only when d functions are included in the Ca basis, it is natural to infer that the d orbitals 'cause' the bending. Hayes has drawn attention¹⁶ to the small s-d energy gap for Ca, the even smaller gap for Ca^+ , and has suggested that participation of d orbitals on Ca could encourage bending; our results provide quantitative support for his qualitative ideas. However, it must be stressed that the bonding in CaF_2 is predominantly ionic (the calculated net charge on Ca is +1.61e); it should also be realized that to look for 'causes' of energy changes as small as 15 cm^{-1} may not be profitable. Chemists are accustomed to explaining molecular shapes with the aid of Walsh diagrams,³ in which orbital energies are plotted as a function of geometry. We display the occupied valence orbital energies for CaF_2 in Figure 2(a) (no d functions on Ca) and Figure 2(b) (five sets of d functions); note that eleven MOs are shown since the Ca 3p-like and F 2s-like orbitals are almost degenerate. If Ca d orbitals are excluded, the six highest MOs are all destabilized on bending. All six are stabilized by the inclusion of Ca d orbitals, though the d participation in the MO is only marginal. Once Ca d orbitals are included, the energies of the five HOMOs increase much less with bond angle. It is not possible to single out one particular MO or interaction as responsible for bending CaF_2 , as the changes induced by the d orbitals in angular energy variations are very similar for all five MOs, which span all four irreducible representations of the C_{2v} point group. It should also be realized that this type of analysis can be misleading,¹⁷ since the sum of the energies of the occupied orbitals does not give the total energy of the molecule as the electron-electron repulsions are effectively counted twice while nuclear repulsion energies are neglected. The space available here does not permit a full discussion of these factors.

We have also performed SCF calculations on several molecules related to CaF_2 . MgF_2 was found to be linear, in agreement with experiment;¹⁸ its bending force constant was calculated to be 0.144 aJ rad^{-2} , and adding d functions to the Mg basis had only a modest effect on that constant, consistent with the large s-d energy separation¹⁶ for both Mg and Mg^+ .

Both CaH_2 and CaCl_2 are also linear, but with very small bending force constants of 0.029 and 0.026 aJ rad^{-2} , respectively. CaCl_2 is known to be linear from experiment,^{2,3} but molecular CaH_2 is not a known species. These results are also consistent with the net charges on Ca of +1.08e in CaH_2 and +1.33e in CaCl_2 . As the net positive charge on Ca increases in the series $\text{CaH}_2 < \text{CaCl}_2 < \text{CaF}_2$, due to the increasing electronegativity of the ligand, the d orbitals on Ca become more available, their contribution to bonding increases, and the tendency towards bending therefore also increases. ScF_2 is predicted to be more acutely bent than CaF_2 , with a bond angle of 129° ; its shape has not been experimentally determined.

DeKock and co-workers have also studied CaF_2 recently,¹⁹ using the Hartree-Fock-Slater approach; while they find CaF_2 to be more strongly bent (130°) than is indicated by our *ab initio* calculations, they agree with us that d orbitals on Ca are responsible for the non-linearity.

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