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Communications

Is CrF_6 Octahedral? Theory Suggests Not!

While SF_6, MoF_6, WF_6, and UF_6 are well-characterized, little is known about CrF_6, since it is thermally unstable and highly reactive;[1,2] indeed, its very existence has just been questioned in a careful experimental investigation.[3] There was little reason to suppose that CrF_6 would differ structurally from the aforementioned octahedral hexafluorides, before a recent theoretical study of several d^0 complexes,[4] which reported that TiH_6^{2-} has a trigonal-prismatic structure of D_{3h} symmetry, while CrH_6 is further distorted to C_{3v} symmetry but CrF_6 is octahedral. We now report high-level ab initio calculations performed with GAUSSIAN86,[5] which strongly suggest that CrF_6 in fact has a trigonal-prismatic structure. We know of *no* other prismatic molecular MX_6 system with monodentate X, with the exception of $W(CH_3)_6$, which was described recently.[6] Even if CrF_6 has not yet in fact been prepared,[3] the question of its shape remains interesting if that shape is predicted to be different from that of other hexafluorides of equal electron count.

In most of this work, a flexible triple-ζ basis A was used; Wachters' 14s9p Cr basis[7] was contracted to 8s5p, extended with an additional p function (exponent 0.15), and then combined with Goddard's 5/3 d basis[8] and Huzinaga's 9s5p F primitives[9] contracted to 5s3p.[10] Gas-phase structures of early-transition-metal fluorides are predicted with high accuracy at the SCF level with this type of basis; calculated[11] r_e bond lengths of 1.695 (equatorial) and 1.734 Å (axial) for trigonal-bipyramidal VF_5 and 1.705 Å for tetrahedral CrF_4 compare well with experimental r_α values[12,13] of 1.704 (5), 1.732 (7), and 1.701 (2) Å, respectively. CrF_5 is Jahn–Teller distorted from a trigonal bipyramid.[14] Calculated bond lengths[11] are close to the average found experimentally,[14] but details of the presumably dynamic distortion have not been unequivocally established, either by experiment or by theory.

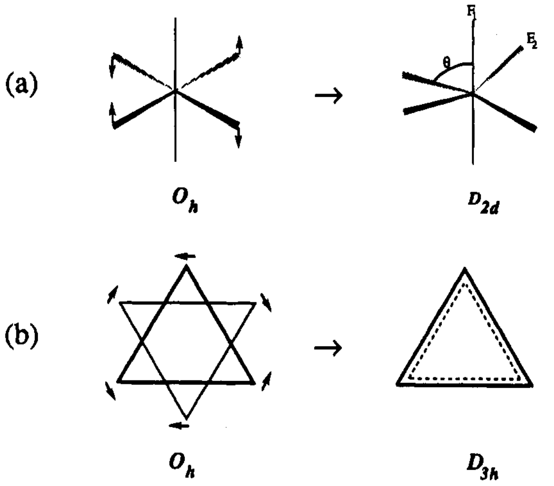

Figure 1. (a) One component of a t_{2u} bending vibration for an octahedral molecule, leading to a D_{2d} structure. (b) Application of all three components of the t_{2u} vibration, resulting in a D_{3h} trigonal prism.

Table I. Calculated Structural Characteristics[a] and Vibrational Wavenumbers[b] for the Three Stationary Points of CrF_6

	O_h	D_{2d}	D_{3h}
$r(Cr-F_1)$	1.6981	1.7003	1.7156
$r(Cr-F_2)$	...	1.6975	...
$\theta(C_3)^c$	(54.7)	...	50.5
θ	(90.0)	87.7	$(79.0)^d$
ω_1	777 (a_{1g})	777 (a_1)	749 (a_1')
ω_2	611 (e_g)	610 (a_1)	529 (a_1')
ω_3	831 (t_{1u})	55 (a_1)	49 (a_1'')
ω_4	270 (t_{1u})	398 (b_1)	818 (a_2'')
ω_5	400 (t_{2g})	830 (b_2)	336 (a_2'')
ω_6	39*i* (t_{2u})	611 (b_2)	817 (e')
ω_7		275 (b_2)	444 (e')
ω_8		831 (e)	387 (e')
ω_9		407 (e)	586 (e'')
ω_{10}		270 (e)	239 (e'')
ω_{11}		51*i* (e)	

[a] Bond distances in Angstroms and bond angles in degrees. See Figure 1 for the definition of the symbols used. [b] In units of cm^{-1}. [c] Angle between a C_3 axis and a Cr–F bond. [d] This angle occurs three times; it links a F atom in one trigonal face to its equivalent in the other face.

The geometry of CrF_6 was initially optimized at the SCF level with octahedral symmetry imposed; the O_h structure is *not a true minimum*, since this theoretical method predicts an imaginary t_{2u} vibrational frequency (39*i* cm^{-1}). With one component of a t_{2u} distortion applied, a D_{2d} structure results, shown in Figure 1a; although marginally more stable (just 3.9 cm^{-1}) than the O_h

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Table II. Calculated Electronic Energies[a] for the Three Stationary Points of CrF_6 and Relative Energies[b] with Respect to the D_{3h} Isomer

geometry	O_h				D_{2d}		D_{3h}	
basis	A		B		A		A	B
SCF	−1639.555 58	+10.9	−1639.540 61	+12.0	−1639.555 60	+10.8	−1639.559 73	−1639.545 18
MP2	−1640.950 87	−67.9	−1640.795 38	−71.0	−1640.950 65	−67.3	−1640.925 02	−1640.768 36
MP3	−1640.511 84	+88.5	−1640.399 38	+84.8	−1640.512 76	+86.1	−1640.545 54	−1640.431 69
MP4DQ			−1640.659 64	−1.1				−1640.659 23
CCD			−1640.556 05	+19.5				−1640.563 47

[a] In atomic units (hartrees). [b] In units of kJ mol^{-1}.

species, it also has an imaginary frequency (e, 51*i* cm^{-1}). When all three t_{2u} components are considered, a D_{3h} structure is obtained (Figure 1b), which is 10.9 kJ mol^{-1} below the octahedral form *and* a true minimum. The Cr–F distance is 0.018 Å longer in the prism than in the octahedron, while the three F atoms on one prismatic face are closer together than in an octahedron. Structural data for these stationary points and calculated vibrational wavenumbers are presented in Table I, with energies in Table II. If it is remembered that vibrational frequencies calculated at the SCF level are generally overestimated by up to 10%,[15] the values predicted for the D_{3h} structure are not inconsistent with the single Cr–F stretching band reported[2] as the IR spectrum of matrix-isolated CrF_6 at 763 cm^{-1}. While Ogden and co-workers[2] naturally assigned this as the t_{1u} mode of an octahedral system, our calculated wavenumbers for the a_2'' and e′ stretching modes for the prismatic structure of 818.2 and 817.4 cm^{-1} differ by only 0.8 cm^{-1}. (Note, however, that Jacob and Willner assert[3] that the band at 763 cm^{-1} is in fact due to CrF_5.)

Geometry optimization at correlated levels was not feasible. All correlated energies were obtained at the SCF geometries optimized with basis A. Corelike orbitals and their corresponding vituals were "frozen". While perturbation theory offers the simplest approach to calculating correlation energies, the MP series unfortunately oscillates pathologically; the MP2 energy is much larger than expected, at −1.3953 au for the octahedral isomer with basis A, and the change from MP2 to MP3 is +0.4391 au! We are unaware of any comparable system for which E3 is so large; the DZ(P)/MP2 energy for SF_6 is −0.8225 au, and E3 is just +0.0335 au. A single-reference description of CrF_6 is therefore poor, and perturbation-based correlated energies are unreliable. The most sophisticated correlated method available was CCD, but as the TZ basis A (125 functions) at this level was computationally too demanding, we adopted a DZ contraction (B, 96 functions) of the same primitives. CCD calculations converged slowly, consuming the equivalent of over 1 CPU-*month* on a Vax 11/780. The CCD margin of stability for the prismatic structure of CrF_6 over the octahedral is 19.5 kJ mol^{-1}, almost double the SCF value. These results strongly suggest that CrF_6 is prismatic, but they are probably not definitive, in view of the oscillations in the MP*n* energies. Kang, Albright, and Eisenstein have reported[4] that CrF_6 is octahedral at the MP2 level; however, their basis was much smaller than ours, and as we have shown that the MP2 method grossly overestimates the correlation energy, we believe their result is unreliable. CrF_6 certainly merits further theoretical and experimental attention.

Why is CrF_6 nonoctahedral, and why is it different from SF_6 or MoF_6? The pseudo-Jahn–Teller approach[16] is helpful; it predicts that if the HOMO–LUMO gap is small enough, distortions away from a symmetrical reference structure may be spontaneous if their symmetry species is contained in the direct product of the HOMO and LUMO representations. For octahedral CrF_6 and MoF_6, the HOMO has t_{1u} symmetry, while the LUMO is t_{2g}; the candidates for pseudo-Jahn–Teller distortions are therefore a_{2u}, e_u, t_{1u}, and t_{2u} species. These distortions are more likely to be associated with bending vibrations than stretching motions, due to the lower energy of the former. Both t_{1u} and t_{2u} bending vibrations are present for octahedral MX_6, but since the t_{2u} mode is invariably at lower frequency than the t_{1u},[17] a t_{2u} distortion may be anticipated for CrF_6. This is exactly the type of distortion predicted by our quantitative calculations. As the HOMO-LUMO gap is smaller for CrF_6 (0.465 au from our SCF results) than for MoF_6 (0.524 au), the pseudo-Jahn–Teller approach[16] predicts a greater tendency to distortion for CrF_6 than for MoF_6. The smaller HOMO–LUMO gap for CrF_6 than MoF_6 is caused both by the strongly oxidizing nature of Cr(VI), which lowers the Cr d orbitals (the t_{2g} LUMO), and by the F··F antibonding interactions, which destabilize the Cr–F nonbonding t_{1u} HOMO (these repulsions increase as the metal–F bond length decreases). For SF_6, with a t_{1g} HOMO, an a_{1g} LUMO, and a fairly large gap between them of 0.813 au, there is no symmetry-allowed pseudo-Jahn–Teller distortion, as there are no t_{1g} vibrations for octahedral MX_6. SF_6 is therefore much more rigidly octahedral than MoF_6; satisfyingly, the t_{2u} bending force constants F_{66} are 1.695[18] and 0.26[19] mdy Å rad^{-2}, respectively, showing the order of rigidity to be $SF_6 > MoF_6 > CrF_6$.

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Steady-State Voltammetry with Microelectrodes: Determination of Heterogeneous Charge-Transfer Rate Constants for Metalloporphyrin Complexes

The kinetics of heterogeneous electron transfer from an electrode to metalloporphyrin complexes in solution has been the subject of a number of publications in this journal and others.[1–6] Attempts have been made to correlate the corresponding standard heterogeneous charge-transfer rate constant, k_s, with the metal

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