On the Structure and Existence of CrF_6

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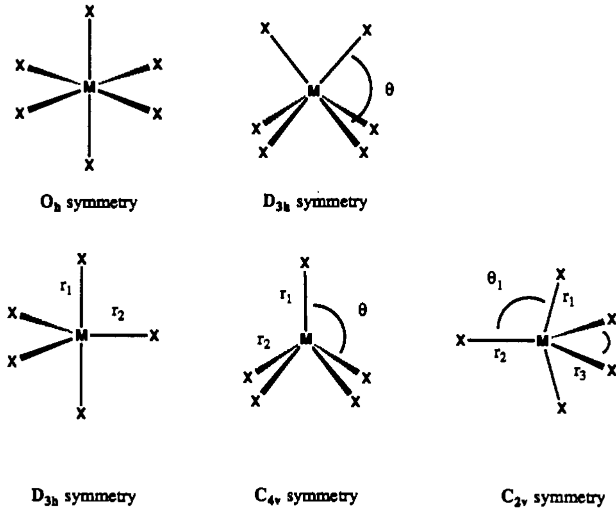
Received June 25, 1992

The structure and existence of CrF_6 are currently hotly debated topics of theoretical[1,2] and experimental[3,4] research. On theoretical side there are conflicting results of quantum chemical calculations as to whether the lowest energy form of CrF_6 is octahedral (O_h)[1] or prismatic (D_{3h}).[2] The disagreement on the experimental side concerns the question if the recorded IR spectrum should be interpreted as evidence for the observation of CrF_6[4] or if it originates from CrF_5.[3] We report theoretically predicted geometries and vibrational spectra for the O_h and D_{3h} forms of CrF_6 using quantum mechanical ab initio methods.[5] In order to estimate the reliability of our data, we report also results for VF_5 and VF_6^- and compare them with experimental data. Examples of MX_6 and MX_9 structures are shown in Figure 1.

Table I shows the calculated energies of the O_h and D_{3h} forms of CrF_6. At the Hartree–Fock (HF) level of theory using the basis set combination I with an effective core potential (ECP) for Cr, the D_{3h} form is predicted to be 3.3 kcal mol^{-1} lower in energy than the O_h form. A similar result was reported by Marsden and Wolynec (MW)[2] using all-electron calculations. The energy difference in favor of the D_{3h} form is reduced to 0.6 kcal mol^{-1} at the HF level when the larger valence-shell basis set combination II is employed (Table I). A dramatic reversal in the stability order is predicted when a set of f-type polarization functions is added to Cr (basis set III). The octahedral form of CrF_6 is 11.2 kcal mol^{-1} *lower* in energy than the D_{3h} form at HF/III.

Earlier theoretical studies of CrF_6 by Kang, Albright and Eisenstein (KAE)[1] were based on second order Møller–Plesset perturbation theory (MP2).[6] KAE reported that the O_h form of CrF_6 is 18.5 kcal mol^{-1} more stable than the D_{3h} form at the MP2 level.[1] However, MW found that the relative energies of the two isomers of CrF_6 are strongly dependent on the order of the perturbation expansion and that the MPn series oscillates pathologically. Table I shows that we find the same ill behavior of the MPn series using pseudopotentials. The O_h form is favored over the D_{3h} form by 17.9 kcal mol^{-1} at MP2 and even by 43.7 kcal mol^{-1} at MP4(SDQ), while the D_{3h} isomer is 16.3 kcal mol^{-1} more stable at MP3. Oscillating results which even appear to diverge rather than to converge have been observed by us in other calculations of transition metal complexes.[7] We agree with MW[2] that the results of KAE[1] which are based on Møller–Plesset perturbation theory are not conclusive, and that MPn data should be used only with care for calculating energies of transition metal complexes.



O_h symmetry D_{3h} symmetry

D_{3h} symmetry C_{4v} symmetry C_{2v} symmetry

Figure 1. Different forms of MX_6 and MX_5 structures.

An alternative method for incorporating electron correlation effects is coupled-cluster (CC) theory,[8a] which has been employed by MW.[2] However, these authors used rather small basis sets (no polarization functions at F), and the CC expansion included only double excitations (CCD).[8b,c] It is now generally accepted that the inclusion of single and in particular triple excitations can be very important when using CC methods. Table I shows the calculated energy differences between the O_h and D_{3h} forms of CrF_6 at the CCD level, at the CC singles and doubles (CCSD),[8d] and at the CCSD(T)[8e,f] level with the latter including a noniterative estimate of the contribution due to triples. We calculated also the energies using conventional configuration interaction with single and double excitations (CISD)[9a] and an estimate of quadruple excitations using the Davidson correction (CISD+Q).[9b] In addition, we present the results obtained by the quadratic CI approach at the QCISD level[10] using basis set combination I.

The results are striking. Without inclusion of triple excitations, the CI and CC methods predict that the higher stability of the D_{3h} form of CrF_6 calculated at the Hartree–Fock level using basis set I is corrected toward the O_h form, but the energy difference between the two forms is small. With the inclusion of the triple excitations the octahedral form is predicted as 11.2

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(5) The calculations have been performed using the program packages Gaussian 90[15] and ACES II[16]. Effective-core potentials with a contracted (3s4p2d) basis set for the valence orbitals[17a] are used for the transition metals and a 6-31G(d) basis set[18a] is used for fluorine. Additional calculations for CrF_6 were carried out using an effective-core potential with a contracted (6s5p3d) basis set for Cr[17b] and a (5s3p2d) contracted basis set for F.[18b] The d polarization functions for F have exponents of 0.81 and 2.42. The f polarization functions for Cr have an exponent of 1.14. The geometry optimizations have been carried out using gradient methods, the vibrational spectra were calculated with numerical second derivatives using the standard methods implemented in Gaussian 90.[15]

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Table I. Theoretically Predicted Geometries and Energies for the Octahedral (O_h) and Prismatic (D_{3h}) Forms of CrF_6

basis set				O_h			D_{3h}		
no.	ECP(Cr)	ECP(F)	method	r (Å)	E_{tot} (hartrees)	E_{rel} (kcal mol^{-1})	r (Å)	angle (deg)	E_{rel} (kcal mol^{-1})
I	(441/2111/41)	6-31G(d)	HF	1.684	–681.80943	0.0	1.699	78.9	–3.3
			MP2		–683.58943	0.0			17.9
			MP3		–683.19528	0.0			-16.3
			MP4 (SDQ)		–683.68461	0.0			43.7
			CISD		–683.02531	0.0			1.8
			CISD+Q		–683.37440	0.0			2.6
			QCISD		–683.46265	0.0			8.8
			CCD		–683.34733	0.0			–0.6
			CCSD		–68.36977	0.0			–0.3
			CCSD(T)		–683.49057	0.0			11.2
II	(6s5p3d)	(5s3p2d)	HF	1.676	–682.68817	0.0	1.690	83.9	–0.6
III	(6s5p3d1f)	(5s3p2d)	HF		–681.72576	0.0			11.2

Table II. Theoretically Predicted and Experimentally Observed Vibrational Spectral Data for CrF_6, VF_5, and VF_6^- with Calculated IR Intensities (km/mol) Placed in Parentheses

CrF_6			VF_5 (D_{3h})		VF_6^- (O_h)	
calcd						
O_h	D_{3h}	exptl	calcd	exptl	calcd	exptl
$r = 1.684$ (Å)	$r = 1.699$ (Å) $\theta = 78.9$ (deg)		$r_{eq} = 1.717$ (Å) $r_{ax} = 1.685$ (Å)	$r_{ax} = 1.734$ (Å)[b] $r_{eq} = 1.703$ (Å)[b]	$r = 1.751$ (Å)	$r = 1.76$–1.81 (Å)[d]
			Values of ν(cm^{-1})			
909 (T_{1u}, 508)	910 (a_2'', 225)	760[a]	950 (e′, 333)	810 (e′)[c]	833 (T_{1u}, 559)	646 (T_{1u})
843 (A_{1g}, 0)	901 (e′, 174)		930 (a_2'', 576)	784 (a_2'')[c]	796 (A_{1g}, 0)	676 (A_{1g})
669 (E_g, 0)	811 (a_1', 0)		859 (a_1', 0)	718 (a_1')[c]		
405 (T_{2g}, 0)	646 (e″, 0)		713 (a_1', 0)	608 (a_1')[c]	639 (E_g, 0)	538 (E_g)
288 (T_{1u}, 51)	533 (a_1', 0)		373 (e″, 0)	336 (e″)[c]		
58*i* (T_{2u})	453 (e′, 4)		369 (a_2'', 25)	331 (a_2'')[c]	363 (T_{2g}, 0)	330 (T_{2g})
	400 (e′, 1)		311 (e′, 31)	282 (e′)[c]	348 (T_{1u}, 31)	300 (T_{1u})
	346 (a_2'', 11)		124 (e′, 3)	110 (e′)[c]	168 (T_{2u}, 0)	
	245 (e″, 0)					
	48 (a_1'', 0)					

[a] References 3,4. [b] Reference 11a. [c] Reference 12a. [d] Reference 11b. [e] Reference 12b.

kcal mol^{-1} more stable than the prismatic form. The energy difference increases by 0.9 kcal mol^{-1} when corrections are made for zeropoint vibrational energies. At the QCISD level, the O_h form is 8.2 kcal mol^{-1} lower in energy than the D_{3h} form. Since the Hartree–Fock calculations using basis set III give another 11.2 kcal mol^{-1} in favor of the O_h form, we estimate that the octahedral form is at least 20 kcal mol^{-1} lower in energy than the D_{3h} form. Thus, theory predicts that CrF_6 has O_h and not D_{3h} geometry as previously suggested.[2]

Table II shows the calculated vibrational frequencies for CrF_6 (O_h and D_{3h}) and the theoretically predicted and experimentally observed geometries[11] and vibrational frequencies[12] for VF_5 and VF_6^-. In agreement with experiment, VF_5 is predicted to have D_{3h} symmetry nad VF_6^- is calculated to be octahedral. The axial V–F bond in VF_5 is calculated as ~0.03 Å shorter than the equatorial V–F bond, which agrees with the experimental result (Table I). The pattern of the calculated vibrational frequencies agree reasonably well with the experimentally observed spectra. The IR-active Cr–F stretching mode of CrF_6 (O_h) is theoretically predicted at 909 cm^{-1}. The experimentally observed IR spectrum[4] shows only one mode at ~760 cm^{-1}. It is known that vibrational frequencies, and particularly stretching modes, are often calculated 10–20% too high.[19] More important than the calculated wavenumbers are the numbers of IR-active fundamentals. A D_{3h} form of CrF_6 should show *two* high-lying IR-active modes separated by ~9 cm^{-1} (Table II). Since only one Cr–F stretching mode is found experimentally[4], the observed species can not correspond to CrF_6 (D_{3h}).

What about the structure and spectrum of CrF_5? Electron diffraction studies indicate a C_{2v} geometry for CrF_5.[13] Preliminary calculations at the ROHF level indicate that the experimental C_{2v} structure is probable, but C_{4v} and D_{3h} forms are very close in energy and cannot be ruled out. More important though are the calculated vibrational spectra which show that CrF_5 should have two different IR active modes separated by 30–40 cm^{-1} which are *not* degenerate as previously assumed.[3] The analysis of the observed splitting for the ^{50}Cr, ^{53}Cr, and ^{54}Cr isotopes in the vibrational spectra of the debated chromium fluoride[4] also rejects the suggestion[3] of a degenerate Cr–F stretching mode.

A final point concerns the calculated bending mode at 288 cm^{-1} (T_{1u}) for CrF_6 (O_h), which is the only other IR-active band (Table II). This mode is predicted to have an IR intensity of ~10% of the Cr–F stretching mode. The bending mode was experimentally observed at ~332 cm^{-1} with a much lower intensity than the stretching mode.[4]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the computer companies Silicon Graphics and Convex. We acknowledge additional computer time from the HLRZ Jülich. G.F. thanks Dr. Colin Marsden for interesting discussions.

Registry No. CrF_6, 13843-28-2.

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