A Density Functional Study of the Structure and Stability of CrF_4, CrF_5, and CrF_6

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The structure and stability of VF_5 and the higher chromium fluorides CrF_4, CrF_5, and CrF_6 have been investigated using density functional theory. The local density approximation (LDA) was used to obtain geometries and vibrational frequencies, while nonlocal corrections were added in order to obtain more accurate binding energies. The results obtained for CrF_4 and VF_5 are in good agreement with the available experimental data, indicating the quality of the method used. Both CrF_5 and CrF_6 are found to be stable with respect to Cr−F dissociation. The calculated binding energies are 49.7 and 40.7 kcal/mol, respectively. In agreement with recent *ab initio* work, the octahedral isomer is found to be the most stable for CrF_6. An activation barries of 16.9 kcal/mol is calculated for pseudorotation to a trigonal prism transition structure. CrF_5 is found to be dynamically Jahn−Teller distorted from D_{3h} to C_{2v} symmetry.

1. Introduction

The structure and existence of CrF_6 has recently been debated rather intensively in the literature, both by experimentalists and theoreticians. The synthesis of CrF_6 was first reported in 1963 by Glemser et al.,[1] who prepared a volatile lemon-yellow material with a Cr:F atom ratio of ca. 1:6 from the reaction of chromium and fluorine at high temperature and pressure. This synthesis was never succesfully repeated, but in 1985, Hope et al.[2,3] prepared a very similar material (yellow, volatile, Cr:F = 1.57) from the fluorination of CrO_3. They also reported a matrix isolation IR spectrum, containing a single band in the stretching region, consistent with an octahedral CrF_6 structure.

The controversy over the structure of CrF_6 started in 1989, with a study of Kang et al.,[4] who argued that certain d^0 systems may be distorted from octahedral symmetry as the result of second-order Jahn−Teller forces. An evidence of this thesis is provided by the $W(CH_3)_6$ molecule, which has been shown[5] by electron diffraction to have a trigonal prismatic structure in the gas phase. The same hypothesis was tested for CrF_6 using MP2/minimal basis calculations, which however predicted an octahedral structure.[4] Yet, somewhat later, a more elaborate theoretical study of Marsden and Wolynec[6] appeared, using slightly larger, but still rather limited, basis sets. They presented MP4 and coupled-cluster (CCD) energies on SCF geometries, and found that the prismatic structure was preferred at both levels of theory.

Meanwhile, there were also new experimental developments. In 1990, new matrix-isolation IR spectra were reported by Jacob and Willner,[7] who asserted that the spectra measured earlier by Hope were actually due to the more stable species CrF_5 rather than CrF_6. Thus the mere existence of CrF_6 was questioned!

As an answer to both the theoretical and experimental studies discussed above, Hope, Levason, and Ogden[8] analyzed their spectra in more detail, stood by their vibrational assignment, and repeated their belief that they had indeed prepared CrF_6 and that its structure must be octahedral, in spite of the contradicting theoretical arguments. However, in response to this study, Jacobs et al.[9] also reconsidered their spectra, in both gas and matrix-isolation phases, and now reported three instead of one band in the stretching region. This observation is clearly incompatible with an octahedral species, but is instead in good agreement with the experimentally known C_{2v} structure of CrF_5. Thus they reaffirmed their conclusion that there is so far no definitive and unambiguous evidence for the existence of CrF_6.

The question regarding the structure of CrF_6 did get an answer in four recent theoretical studies,[10−13] performed with extended basis sets, including f-type polarization functions for Cr. Different methods were used, the most elaborate being the recently developed CASPT2 method[14] and the coupled-cluster CCSD(T) method. A consensus was reached in that all four studies favor the octahedron over the trigonal prism, although strongly different results were obtained for the energy difference between the octahedral and prismatic forms, varying from 14.4 to 49.9 kcal/mol.

Although the results from these studies are conclusive in that they preclude the existence of a stable trigonal prismatic structure for CrF_6, they do not provide information on the more stringent question as to whether octahedral CrF_6 can exist as a stable molecule in the gas phase and has ever actually been prepared. Vibrational frequencies for octahedral CrF_6 were presented, but the results were obtained at the Hartree−Fock level, which is known[15] to overestimate stretching frequencies

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by up to 20%. With the largest basis sets used, Marsden, Moncrieff, and Quelch (MMQ)[13] predict harmonic frequencies of 850 and 329 cm^{-1} for the IR-active modes of isolated octahedral CrF_6. As the authors—somewhat inconclusively—comment, these results "agree about as well as could be expected" (from Hartree−Fock) with the matrix result for CrF_6 (763 cm^{-1}) obtained by Hope et al.[2,3]

In the present study we present a detailed analysis of the structure and stability of CrF_6, CrF_5 and CrF_4, using density functional theory (DFT). The local density approach (LDA) was used to obtain geometries and vibrational frequencies. This method has recently been found to predict accurate geometries and vibrational frequencies of a range of transition metal compounds containing (among others) halogen ligands.[16] In order to obtain more reliable binding energies nonlocal corrections were added perturbatively, using the LDA optimized geometries. Apart from the chromium fluorides VF_5 was included as a test case in the present calculations. Both VF_5 and CrF_4 are experimentally well-known, and the results obtained for these two molecules will serve as a guideline for the reliability of the results obtained for CrF_5 and CrF_6.

2. Computational Details

The present calculations were performed using the DMol program.[17] Geometries and vibrational frequencies were obtained using the local density (LDA) approximation where the exchange-correlation functional was approximated using the Vosko, Wilk, and Nusair (VWN) potential.[18] In order to obtain more reliable bond energies, a nonlocal gradient correction to the exchange energy was evaluated, using the final LDA geometries and electron densities. Here, the exchange potential proposed by Becke[19] was used. Unfortunately, inclusion of a nonlocal (NL) correction to the correlation energy is not available in DMol, when using the VWN approximation at the LDA level. However, it has been found that the largest effect to the binding energy comes from the nonlocal correction to the exchange contribution, whereas the influence of the nonlocal correction to the correlation term is rather modest.[20] The binding energies in DMol are calculated relative to spherical spin unrestricted atoms.

DMol uses numerical functions for the atomic basis sets. The atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. The radial portion of the grid is obtained from the numerical solution of the atomic DFT equations. All calculations in this work were performed using a double numerical basis set augmented by polarization functions (DNP), which compares in size to a double-ζ plus polarization basis set.

The evaluation of various integrals is accomplished by a numerical integration procedure. The integration points are generated in a spherical pattern around each atomic center. The number of radial points N_R used is given as

$$N_R = 1.2 \times 14(Z + 2)^{1/3} \qquad (1)$$

where Z is the atomic number. The maximum distance for any function is 12 au. Angular integration points are generated at each of the N_R points, creating shells around each nucleus. The number of angular points ranges from 14 to 302, depending on the behavior of the density.

For the calculation of the Coulombic potential, a model density obtained by a projection scheme is used. The multipolar fitting functions for this density were all generated by using an angular momentum number 1, one larger than that in the atomic basis set.

Geometries were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS)[21−24] algorithm. The structure was considered coverged when the largest gradient was less than 5 × 10^{-4}. Frequencies were computed by finite differences of the first derivatives. A two-point (or central) differencing was carried out with a step size of 0.01 au.

Table 1. Geometrical Parameters (in Å) and Vibrational Frequencies (in cm^{-1}) of CrF_4

	LDA	exptl
r(Cr−F)	1.704	1.706(2)
ν_1 (a_1)	717	717 ± 3
ν_2 (e)	179	<200
ν_3 (t_2)	798	790
ν_4 (t_2)	168	201

3. Results and Discussion

3.1. Molecular Structure and Vibrational Spectra. 3.1.1. CrF_4. Chromium tetrafluoride is an experimentally well-known molecule. Its molecular structure has been determined by gas-phase electron diffraction and was found to be tetrahedral with a Cr−F distance of 1.706(2) Å.[25] The ground state corresponds to the highest d^2 multiplicity: $^3A_2$.[26] The calculated LDA results for CrF_4 are shown in Table 1. Optimization of the bond lengths yields a Cr−F distance of 1.704 Å, which is in good agreement with the experimental result. The CrF_4 normal modes of vibration belong to the following irreducible representations: $a_1 + e + 2t_2$, with the t_2 modes infrared active. The t_2 fundamentals are calculated at 798 and 168 cm^{-1} respectively. While the stretching band of 798 cm^{-1} compares very well with the experimental[9] result of 790 cm^{-1}, the t_2 bending mode is underestimated by 32 cm^{-1}. This is conform with the observation made in previous studies[16] on analogous tetrahedral molecules ($TiCl_4$, $ZrCl_4$, $Ni(CO)_4$) using numerical basis sets. It was found there that the results for the bending modes are very sensitive to the orientation of the tetrahedral molecule and to the grid used.[27] In all cases, the calculations underestimated the lowest bending mode. All other calculated wavenumbers are seen to be in close agreement with experiment. The wavenumber of the infrared inactive mode ν_1 was deduced from the combination $\nu_1 + \nu_4$. Its estimated position, 717 cm^{-1} is exactly reproduced by our calculations. The ν_2 band could not be detected in the IR spectrum, but was expected[9] to be below 200 cm^{-1}. Our calculations predict it at 179 cm^{-1}.

3.1.2. VF_5 and CrF_5. VF_5 is a formally d^0 system, with a closed-shell ground state. An electron diffraction study[28] points to a D_{3h} structure, with axial and equatorial V−F distances of 1.732(7) and 1.704(5) Å, respectively. However, IR spectroscopic studies[29−31] have indicated that the barrier for a Berry pseudorotation process proceeding from the D_{3h} to a C_{4v} transition structure is very low. An analysis of the ν_7(e′) vibrational transitions puts the barrier height at 1.2−1.5 kcal/mol.

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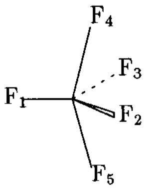
Table 2. Geometrical Parameters (in Å) (Distances) and deg (Angles) of the $^2A_2$ and the $^2B_1$ States of CrF_5

	LDA		
	$^2A_2$	$^2B_1$	exptl
$r(Cr-F_4) = r(Cr-F_5)$	1.742	1.742	1.742
$r(Cr-F_1)$	1.682	1.698	1.696
$r(Cr-F_2) = r(Cr-F_3)$	1.697	1.686	1.696
$\angle F_1CrF_4 = \angle F_1CrF_5$	91.4	89.3	95.8
$\angle F_1CrF_2 = \angle F_1CrF_3$	121.8	117.4	115.9

Both the D_{3h} and C_{4v} structures were optimized at the LDA level. For the D_{3h} structure, bond distances of 1.746 and 1.712 Å were obtained. Conform with the electron diffraction results, the calculated axial V−F distance is about 0.03 Å longer than the equatorial V−F distance. For the C_{4v} structure, our calculations indicate a significantly shorter axial than equatorial V−F distance. The calculated values are 1.692 and 1.735 Å for the axial and equatorial V−F bond respectively, with an $F_{ax}VF_{eq}$ bond angle of 105.4°.

From the frequency analysis, the D_{3h} structure is found to be a stable minimum, while for the C_{4v} isomer one imaginary mode of b_2 symmetry is calculated, carrying the square pyramid back into the more stable trigonal bipyramid. The barrier height for pseudorotation is found to be 1.9 kcal/mol at the LDA level. Including nonlocal corrections only slightly modifies this value, to 2.0 kcal/mol. A slightly lower barrier, 0.7 kcal/mol, was found in a recent MP2 study.[12] On the whole, the results obtained for VF_5 with the present DFT method should be considered as very satisfactory.

An electron-diffraction investigation of the structure of gaseous CrF_5 (d^1 system) has indicated that this molecule is slightly distorted from D_{3h} to C_{2v} symmetry.[32] This distortion can be rationalized in terms of the Jahn−Teller instability of the $^2E''$ degenerate ground state arising from a d^1 configuration in a trigonal prismatic environment. Symmetry arguments indicate that the Jahn−Teller active vibration is of e′ symmetry, carrying the nuclei over into a C_{2v} distorted configuration—in agreement with the epikernel principle.[33] Thereby the $^2E''$ state reduces to $^2A_2 + {}^2B_1$. To our knowledge, no previous theoretical calculations on this system have been performed before. In the present work, both the $^2A_2$ and $^2B_1$ states were optimized. The resulting geometries are shown in Table 2. The F atoms are labeled according to the following structure:



In this scheme, F_1 is situated on the C_{2v} twofold axis, while F_2,F_3 and F_4,F_5 denote symmetry-equivalent pairs of equatorial and axial ligands respectively. We note however that for each of the minimum energy structures obtained two other equivalent structures can be drawn, with the role of the F_1 ligand taken over by one of the other equatorial ligands of the trigonal prism. Thus a two-dimensional "Mexican hat"-like Jahn−Teller surface is obtained, with the trigonal bipyramid as the central pivot point and six surrounding minima with alternating $^2B_1$ and $^2A_2$ symmetry.

Table 3. Geometrical Parameters (in Å) and Vibrational Frequencies (in cm^{-1}) of VF_5 and CrF_5

	VF_5		CrF_5	
	LDA	exptl[a]	LDA	exptl[b]
$r(M-F_{ax})$	1.746	1.732(7)	1.739	1.732(8)
$r(M-F_{eq})$	1.712	1.704(3)	1.692	1.689(5)
ν_1 (a_1')	720	719	716	696[c] (a_1)
ν_2 (a_1')	623	608	622	603[c] (a_1)
ν_3 (a_2'')	792	784	787	768 (b_1)
ν_4 (a_2'')	314	331	313	332 (b_1)
ν_5 (e′)	820	810	828	792 (b_2) 755 (a_1)
ν_6 (e′)	261	282	272	284[c] (b_2) ... (a_1)
ν_7 (e′)	106	109	129	261[c] (b_2) ... (a_1)
ν_8 (e″)	323	336	311	216[c] (b_1) ... (a_2)

[a] Distances from ref 28; frequencies from ref 30. [b] Distances from ref 32; frequencies from ref 9. [c] Tentative, deduced from combinations.

As one can see, the optimum geometries are only slightly distorted from D_{3h} symmetry. In both cases, a significantly larger bond distance is found for the axial than for the equatorial Cr−F bonds, in perfect agreement with the distances reported from experiment. Our calculations further indicate that $^2B_1$ and $^2A_2$ have almost exactly the same energies at their respective minimum energy geometries. At the local level, the $^2A_2$ state is found to be the most stable, with the $^2B_1$ state situated 0.9 kcal/mol higher in energy. However, with the addition of a nonlocal correction the ordering of both states is reversed, with the $^2B_1$ state now becoming the most stable and $^2A_2$ situated at 0.7 kcal/mol. Thus our results suggest that the "Mexican hat" potential surface of CrF_5 is very flat, so that rotation on this surface can occur with very little input of energy. As a consequence, a direct comparison between the calculated and experimental bond angles in Table 2 becomes somewhat arbitrary, in view of the fact that the experimental bond angles were determined by fitting the electron-diffraction data to a C_{2v} "static" model.

The calculated vibrational frequencies for VF_5 and CrF_5 are shown in Table 3. A calculation of the vibrational frequencies for the individual $^2A_2$ and $^2B_1$ C_{2v} states of CrF_5 turned out to be unfeasible, due to severe convergency problems. Instead we decided to perform a calculation on an "average" $^2E''$ state within D_{3h} symmetry, obtained by occupying each of the components of the HOMO e″ level with half an electron. A geometry optimization (within D_{3h} symmetry) was performed first, resulting in a Cr−F bond distance of 1.739 Å for the axial and 1.692 Å for the equatorial bonds, again very close to the experimental bond distances. We realize of course that the accuracy of the calculated frequencies will somehow be impaired by the procedure used, especially of the e′ bending mode involved in the Jahn−Teller distortion. In fact, since all calculated frequencies are real, a stable minimum is found for the average $^2E''$ state within D_{3h} symmetry, whereas a calculation on the "true" $^2E''$ state would have to indicate a saddle point, with an imaginary frequency for the lowest e′ mode. However, from a comparison of the predicted vibrational wavenumbers for VF_5 and CrF_5 it should still be possible to obtain some valuable information for the interpretation of the experimental CrF_5 spectrum.

Pentafluorides of D_{3h} symmetry should have eight normal modes with species designations: $2a_1' + 2a_2'' + 3e' + e''$. Looking first at the results obtained for VF_5 (Table 3), we notice that the calculated results agree very well with the experimental fundamental frequencies, with a maximum discrepancy of 21

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cm^{-1}. All stretching modes are calculated slightly too high, while for the bending modes the values obtained are too low. The LDA results obtained from this study are clearly superior to the results obtained from a recent SCF study on VF_5,[12] producing values which are uniformly larger than the experimental values, with a mean 7.2% error. Our results do agree very well with another numerical LDA study,[16] performed using an alternative (von Barth−Hedin) functional for the exchange-correlation potential.

Both the IR spectrum of VF_5 and CrF_5 are characterized by two intense bands in the stretching region. The five stretching modes of VF_5 are distributed among $2a_1' + a_2'' + e'$, of which a_2'' and e' are infrared active. Both represent asymmetric stretching modes, of the axial (a_2'') and equatorial (e') V−F bonds respectively. The two intense bands in the IR spectrum of VF_5, found at 784 and 810 cm^{-1}, can thus be easily assigned as the a_2'' and e' stretching modes. Their relative position is conform with the fact that the axial V−F bonds are longer than the equatorial bonds. Comparable bands are found at 768 and 792 cm^{-1} in the IR spectrum of CrF_5. The agreement between the calculated frequencies, 787 and 828 cm^{-1}, and the experimental band positions is significantly worse than for VF_5, but still acceptable considering the fact that the actual symmetry of CrF_5 is only C_{2v}. Lowering the D_{3h} symmetry of VF_5 to the C_{2v} symmetry of CrF_5 removes the degeneracy of each e mode, resulting in a split into a and b modes. The five stretching modes now belong to $3a_1 + b_1 + b_2$, which are all symmetry-allowed. Of these, the b modes are expected to have high intensities in the IR spectrum, and the two intense bands have therefore been assigned as the b_1 $Cr-F_{ax}$ and b_2 $Cr-F_{eq}$ asymmetric stretching modes. It should be noted that it is actually the band at 768 cm^{-1} which has been the subject of recent debate in the literature. It is a very intense band, with a well-defined chromium isotopic structure which has been attributed by Hope et al.[2,3,8] to the t_{1u} stretching mode of octahedral CrF_6. Their proposal is rejected by the authors of ref 9, on the basis of the presence of the additional band at 792 cm^{-1} in the stretching region. This band is extremely broad and therefore has a fairly low absorbance, which is, according to ref 9, the reason why it was overlooked by Hope et al. The unusual broad appearance of the band has been explained as being due to coupling with pseudorotation motions. This explanation is confirmed by our calculated results for CrF_5, indicating indeed the presence of a dynamic Jahn−Teller effect.

In the deformation mode region of the CrF_5 IR spectrum, only one band, which exhibits a chromium isotopic pattern, is observed at 332 cm^{-1}. In comparison to VF_5, showing a similar band at 331 cm^{-1}, the band is assigned to the out-of-phase bending mode of the equatorial bonds, with symmetry a_2'' in D_{3h} and reducing to b_1 in C_{2v}. Our calculations confirm the assignment: the a_2'' bending vibration is indeed calculated at about the same wavelength for both molecules.

3.1.3. CrF_6. Table 4 shows the calculated results for the structure and vibrational frequencies of CrF_6. An optimization was performed for both the O_h and D_{3h} geometries. Conforming with the most recent *ab initio* studies,[10−13] we find the octahedron to be more stable than the trigonal prism. At the LDA level, the calculated energy difference between both structures equals 15.0 kcal/mol. Adding a nonlocal correction increases this energy difference further to 16.9 kcal/mol. This result is much more in line with the most recent CCSD(T) result of 14.2 kcal/mol obtained by Marsden et al.[13] than with the much higher CASPT2 result of 49.9 kcal/mol from Pierloot and Roos.[10]

Table 4. Geometrical Parameters (in Å) and Vibrational Frequencies (in cm^{-1}) of the O_h and the D_{3h} Isomers of CrF_6

	LDA O_h		LDA D_{3h}
r(Cr−F)	1.728		1.737
ν_1 (a_{1g})	699	ν_1 (a_1')	685
ν_2 (e_g)	603	ν_2 (a_1')	481
ν_3 (t_{2g})	347	ν_3 (a_2'')	774
ν_4 (t_{2g})	144	ν_4 (a_2'')	361
ν_5 (t_{1u})	771	ν_5 (e')	756
ν_6 (t_{1u})	324	ν_6 (e')	406
		ν_7 (e')	363
		ν_8 (e'')	545
		ν_9 (e'')	222
		ν_{10} (a_2'')	111 *i*

The calculated Cr−F bond lengths at the LDA level are 1.728 Å for the O_h structure and 1.737 Å for the D_{3h} structure. Previous geometry optimizations on CrF_6 have been performed at the SCF level,[6,11,13] and at the correlated level using CASPT2[10] or SDQ-CI.[34] For the latter, an octahedral geometry was assumed. The LDA results for the bond lengths are considerably longer than all previously obtained SCF results. With their largest basis sets (denoted as basis F in ref 13), Marsden et al. found an SCF Cr−F distance of 1.678 Å for the octahedron and 1.693 Å for the trigonal prism. At the correlated level larger distances are obtained. A value of 1.747 Å was calculated for the octahedron by Miyoshi et al.,[34] using SDQ-CI. At the CASPT2 level, an even larger Cr−F distance of 1.754 Å was found for the O_h isomer, while the CASPT2 result obtained for the prigonal prism, 1.727 Å, is slightly shorter than the present LDA result. On the basis of the results obtained for CrF_4, VF_5, and CrF_5, we would expect the present LDA results for the bond lengths to be accurate to within at least a few hundreds of an Å.

The transition state character of the trigonal prism is confirmed by the results of a frequency analysis (see Table 4), showing one imaginary frequency for the D_{3h} optimum. The corresponding a_1'' vibration transforms the D_{3h} structure to the octahedral form by rotating one triangular F_3 face relative to the other.

The vibrational frequencies calculated for the octahedron are all real. Of the six normal modes ($a_{1g} + e_g + 2t_{1u} + 2t_{2g}$) to be expected for an octahedral hexafluoride species, only the t_{1u} modes are infrared active. An infrared spectrum of octahedral CrF_6 should therefore exhibit two bands, one in the stretching and one in the bending region. In the spectrum recorded by Hope et al.[2,3,8] an intense absorption is indeed observed in the Cr−F stretching region at ca. 760 cm^{-1}. The absence of any additional bands (see however the discussion of the CrF_5 spectrum) was used as an argument for attributing the recorded spectrum to octahedral CrF_6. The position of the t_{1u} stretching mode is indeed almost exactly reproduced by our calculations, placing it at 771 cm^{-1}. No band was found in the bending region of Hope's spectrum, but the t_{1u} bending mode was estimated to lie in the frequency region 250−300 cm^{-1}. Our calculations predict it at 324 cm^{-1}. However, it should be noted that the calculated results for the infrared active modes in CrF_6, 324 and 771 cm^{-1}, also correspond almost exactly to the positions of the two most intense bands in the spectrum recorded by Jacobs et al.,[9] 332 and 768 cm^{-1} (see Table 3), where they were assigned to the b_1 modes of CrF_5. As far as these two bands are concerned, our calculations indeed predict almost exactly the same IR spectrum for both molecules. The question whether or not a third band is present in the experimentally

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Table 5. Total Binding Energy (in kcal/mol) of CrF_x ($x = 1-6$), Relative to Spherical Spin-Unrestricted Atoms

structure		LDA	LDA/NL	exptl
CrF		132.9	115.7	106
CrF_2		259.8	227.3	227
CrF_3		410.9	351.8	356
CrF_4		526.8	440.0	
CrF_5	$^2A_2$	607.4	489.0	
	$^2B_1$	606.5	489.7	
CrF_6	O_h	675.1	530.4	
	D_{3h}	660.1	513.5	

recorded spectrum is therefore of crucial importance for the assignment of the spectrum to either CrF_5 or CrF_6.

3.2. Energetics. The calculated total binding energies of CrF_4, CrF_5, and CrF_6, relative to spin-unrestricted atoms, are shown in Table 5. We have also included in this table results obtained for the lower binary fluorides CrF, CrF_2, and CrF_3. For these systems, experimental binding energies have been reported,[35] and the agreement with the computed values serves as an indication for the reliability of the results obtained for CrF_4, CrF_5 and CrF_6.

As found in previous DFT studies[20,36,37] all binding energies are grossly overestimated at the local level. Indeed, the addition of a nonlocal gradient correction to the exchange energy decreases the result obtained for the binding energies by 16−24 kcal/mol per Cr−F bond. At the nonlocal level, the agreement between the calculated total binding energies for CrF_2 and CrF_3 and experiment is excellent, with errors less than 5 kcal/mol. However, the error obtained for CrF is significantly larger. Even at the nonlocal level, the Cr−F dissociation energy is still overestimated by almost 10 kcal/mol. On the other hand, the dissociation energy of one fluorine from CrF_2 is underestimated by the same amount.

Both CrF_5 and CrF_6 are found to be stable with respect to dissociation into F and the corresponding lower chromium fluoride, although a significantly lower Cr−F bond dissociation energy is obtained for CrF_6, 40.7 kcal/mol, than for CrF_5, 49.7 kcal/mol. The calculated result for CrF_5 compares rather well to the experimental value of 46 kcal/mol reported in ref 9. No experimental information is available regarding the Cr−F bond dissociation energy of CrF_4 and CrF_6. The calculated result for CrF_4 is 88 kcal/mol. These results clearly indicate that the higher binary chromium fluorides considered here are all considerably less stable toward Cr−F dissociation than the lower binary fluorides CrF, CrF_2, and CrF_3.

Finally, for the disproportionation reaction

$$2CrF_5 \leftrightarrow CrF_6 + CrF_4$$

a reaction energy of 9.0 kcal/mol is calculated at the nonlocal level. Of course nothing is said from the present calculations regarding the activation barrier of the considered reaction. Nevertheless, the result obtained for the reaction energy seems to suggest that CrF_6 might be unstable in the presence of CrF_4, to which it may pass one fluorine atom in order to generate two CrF_5 molecules.

4. Conclusion

We have presented results from a DFT study on VF_5 and the binary chromium fluorides CrF_4, CrF_5, and CrF_6. The results obtained for VF_5 and CrF_4 have indicated that highly accurate results for the structures and vibrational frequencies are obtained already at the LDA level. Inclusion of nonlocal corrections is imperative for an accurate determination of binding energies. Its effect on the relative energy of the different calculated isomers is however rather modest.

Conform with the experimental results, VF_5 is found to be trigonal prism, although the barrier for pseudorotation via a C_{4v} transition state is very low (2 kcal/mol at the nonlocal level). CrF_5 is shown to be dynamically Jahn−Teller distorted from D_{3h} to C_{2v} symmetry. Our calculations indicate that the molecule is in fact free to rotate on the “Mexican hat” Jahn−Teller surface connecting the different C_{2v} minima. This may explain the unusual broad appearance of the band at 792 cm^{-1} in the IR spectrum recorded by Jacobs et al.[9]

For CrF_6, our calculations confirm the results obtained from recent *ab initio* studies. Its optimum geometry is found to be octahedral, with an activation barrier of 16.9 kcal/mol for rotation to a D_{3h} transition structure. The molecule is found to be rather stable to Cr−F dissociation, but may react with CrF_4 to form two CrF_5 molecules.

Even though the present study may not have been able to provide a conclusive answer to the question whether or not CrF_6 can exist as a stable molecule in the gas phase, we hope that the results of our calculations will be helpful in its possible identification.

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