

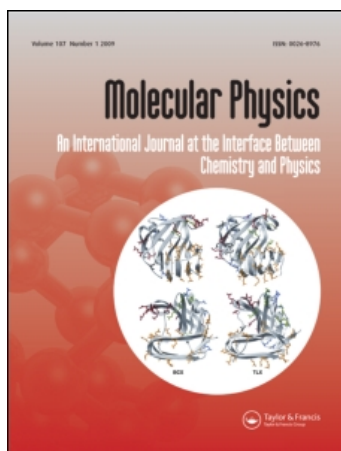
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Molecular Physics

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713395160>

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To cite this Article Wright, Timothy G. and Lee, Edmond P. F.(1993) '*Ab initio* studies of X_3^- and X_3 ($X=F, Cl$)', Molecular Physics, 79: 5, 995 – 1009

To link to this Article: DOI: 10.1080/00268979300101781

URL: <http://dx.doi.org/10.1080/00268979300101781>

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Ab initio studies of X_3^- and X_3 ($X=F, Cl$)

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(Received 14 July 1992; accepted 3 November 1992)

The electronic structures, optimized geometries and harmonic vibrational frequencies of F_3^- , Cl_3^- , F_3 and Cl_3 have been studied by *ab initio* calculations, using various basis sets and different correlation methods, including MP2, CISD and CASSCF. For the anions, reasonably consistent results were obtained for the closed-shell singlet ground states. However, for the open-shell doublet states of the neutral trihalogens and the triplet states of the anions the optimized geometries and hence the computed harmonic vibrational frequencies were found to be rather basis set and method dependent. Calculations based on a single configuration are inadequate for the neutral trihalogens, and the electronic structures of the various open-shell states of both the neutral trihalogens and their anions are rather complex. The different effects due to basis set size and dynamic and non-dynamic electron correlation on the various electronic structures, optimized geometries and computed harmonic vibrational frequencies obtained are discussed. Comparison with experimental data was made where available.

1. Introduction

The trihalogen anions, X_3^- , have been studied experimentally by various methods, including: infrared and Raman spectroscopy on matrix-isolated species [1–3]; thin layer solid and solution infrared and Raman spectroscopy [4]; electronic absorption spectroscopy (reference [5] and references therein); nuclear quadrupole resonance (NQR) spectroscopy [6]; and Mössbauer spectroscopy [7]. However, the experimental evidence for the existence of the trihalogen radical complexes, X_3 , is less strong. A ‘stationary state’ of Cl_3 has been assumed in a number of studies on atomic Cl recombination kinetics [8] and some mixed trihalogen complexes were considered as intermediates in the mechanism of interhalogen exchange reactions in a molecular beam kinetics study [9]. An earlier identification of Cl_3 in a matrix by infrared spectroscopy [10] has been reassigned by later work to be Cl_3^- [11,12]. Recent studies have postulated the existence of Cl_3 in the laser-induced luminescence spectra of the products from the photodissociation of Cl_2 under collision conditions [13,14]. In addition, Br_3 and Br_3^- have been observed by matrix Raman spectroscopy [15].

The theoretical studies that have been performed are largely on the lighter species X_3 and X_3^- , i.e. $X = Cl$ or F . Potential energy surfaces for the $X_2 + X$ systems have been studied by the Monte Carlo trajectory method [16] and valence-bond diatomics-in-molecules (DIM) method [17]. Various calculational methods such as a qualitative MO picture [18], semi-empirical [19], valence-bond pseudopotential [20], local density functional [21] and *ab initio* calculations [22–28] have been carried out to study the equilibrium geometries, vibrational frequencies and electronic structures

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of X_3^- and, to a lesser extent, X_3 . The highest level of *ab initio* geometry optimizations performed were the TZP/ACCD [23], 6-31+G*/MP2 [25] and DZ+s*/MP2 [27] calculations on F_3^- , HF/[5s4p] calculations on Cl_3^- [22] and the MRCI calculations of Sannigrahi and Peyerimhoff [28] on Cl_3 . For the last mentioned study, a C_{2v} structure was assumed in a point-by-point geometry optimization. At the time when the manuscript of the present work was in preparation, a SCF/MPn/CCSD/QCISD study on F_3^- using various basis sets (the largest being a TZ2Pf+ basis set) appeared [29]. In general, the conclusions from this latest study are similar to those here for this species, particularly the importance of multireference character (see later text). However, all the above-mentioned studies have dealt only with a single spin-symmetry state (usually an unspecified state), which was assumed to be the ground state. In some cases (e.g., references [28] and [29]), a linear and/or symmetrical structure seems to have been assumed in the geometry optimization; also, the optimized geometries and/or vibrational frequencies at the correlated level were sometimes obtained by interpolation of energies with a polynomial/parabola fit [24,26,28,29] rather than by evaluating the energy gradients and/or second derivatives. On the whole, it is therefore felt that there is still a lack of a systematic computational study on both X_3^- and X_3 (where $X = F, Cl$), which is part of the aim of the present investigation.

It was intended to carry out full geometry optimization making use of analytical derivative methods as much as possible and to examine the effects of basis set size and dynamic and nondynamic electron correlation on the optimized geometries and harmonic vibrational frequencies of low lying states of both X_3^- and X_3 , where $X = F$ and Cl . It was also intended that a consistent and compatible approach should be used in dealing with both the open- and closed-shell electronic states to be studied. Some difficulties were encountered, particularly for F_3 , and these will be discussed.

2. Computational details

Standard basis sets of the split-valence type and standard polarization functions were used throughout [30,31], and do not require further description. For Cl , the largest basis set used was a [9s6p] [32] plus a set of d polarization functions [30] (each used as set of six Cartesian functions), which is of triple zeta plus polarization (TZP) quality and is comparable with the 6-311G* basis used for F . Diffuse functions were taken from reference [33]. All SCF calculations at the Hartree–Fock level were restricted-spin type for both open- and closed-shell electronic states. At the MP2 level, however, UMP2 calculations were carried out for open-shell species, as analytical gradients of ROMP2 energies for an open-shell wavefunction were unavailable (all electrons and orbitals were included in the (U)MP2 calculations). Spin-projected (PUMP2) calculations were also performed in some cases at the respective optimized UMP2 geometries. However, in cases where spin contamination was small, the calculated PUMP2 and UMP2 energies at the same geometry (usually the UMP2-optimized geometry) were not too different, about $0.005 E_h$ ($E_h = \text{hartree} \approx 4.359\,748\,2 \times 10^{-18} \text{ J}$) and therefore will not be further discussed.

The (U)MP2 method may be considered as the most cost effective electron correlation method for systems where a single-determinantal wavefunction is adequate. However, in cases of open-shell electronic states where spin-contamination is high, UMP2 calculations will be of little value. This is usually the case when non-dynamic electron correlation is important (see later text). Consequently, some other

electron correlation methods have to be used. Geometry optimization and force constant calculations using the single-reference CISD method, including all electrons and all MOs, were performed only on the closed-shell singlet states of X_3^- , as analytical gradients of CISD energy were available only for closed-shell wavefunctions. Some single-point CISD calculations on some selected states of X_3^- were also performed and the reason for their choice will become apparent in the later text. In addition, CASSCF calculations including all valence p electrons and all valence p orbitals, which are essentially full CI calculations of 15-/16-electrons in 9 MOs, were also carried out both for X_3 and X_3^- , respectively. As well as the fact that these CASSCF calculations would account for non-dynamic electron correlation effects, they were the only method which was successful for some states of X_3 , where other levels of calculation were unable to obtain convergence in the energy iteration procedure and/or geometry optimization. For some electronic states, however, there were also persistent convergence problems in the CASSCF energy procedure during the geometry optimization, showing that the electronic structures of these states are rather complex.

For geometry optimizations, analytical gradients were used throughout. All initial geometries used had a C_s symmetry and full geometry optimization was carried out, unless otherwise stated. In some cases where either one initial geometry failed to converge or another possible geometry which differs from the optimized geometry already obtained was suspected, different initial geometries were chosen to search for a possible lower minimum. When a higher symmetry, such as a C_{2v} or a linear point group (subsequently run under C_{2v} or D_{2h} symmetry) became apparent, a new geometry optimization was carried out using the new symmetry point group (however, in the tables, the bond lengths in the lower point group are given; these may not be exactly the same due to the practical necessity of using a non-zero tolerance on the geometry optimization). In such cases, the difference in the computed energies at the respective optimized geometries between using the different point groups is usually small, except that for CASSCF calculations where the size of the configurational space is comparatively small and the reduction of the configurational space due to a higher point group gave a noticeably higher computed energy as compared with that using a lower point group. Such observations in the CASSCF calculations are also due to the fact that the CASSCF energy surfaces are rather complex, as will be discussed later. Analytical second derivative calculations, which gave harmonic vibrational frequencies, were possible only for RHF energies of both open- and closed-shell wavefunctions, and MP2 energies for closed-shell RHF wavefunctions. For UMP2, CISD and CASSCF, numerical second derivatives were used throughout.

Most RHF and all MP2 calculations were carried out using Cadpac [34]; all single-geometry CISD energy and all CASSCF calculations, using Gamess [35]; and all CISD gradients and frequencies calculations, using Gaussian 90 [36].

3. Results and discussion

3.1. F_3^-

The calculated results for the singlet, closed-shell state are given in table 1. Agreement between them and those available in the literature is, in general, very good. The effects of basis variation on the various computed quantities obtained will be examined first. At the HF level, the optimized geometry was found to be

Table 1. Calculated energies, optimized geometries and vibrational frequencies of the F₃⁻ molecule (closed-shell singlet).

Method	Basis set	Energy/ <i>E</i> _h	<i>r</i> ₁ / <i>a</i> ₀ ^a	<i>r</i> ₂ / <i>a</i> ₀	θ deg	ν ₁ /cm ⁻¹	ν ₂ /cm ⁻¹	ν ₃ /cm ⁻¹
SCF	4-31G	-297.75206	3.142	3.142	180	453	352	593
	4-31G*	-297.76700	3.729	2.703	180	283	224	810
	6-31G*	-298.04704	3.814	2.678	180	265	222	855
	6-31+G*	-298.11044	4.553	2.580	180	222	179	898
	6-311G*	-298.14897	4.406	2.609	180	154	128	1135
	6-311+G*	-298.18877	4.715	2.543	180	133	106	1124
MP2	4-31G	-298.18633	3.334	3.334	180	408	267	769
	4-31G*	-298.36322	3.249	3.249	180	436	290	767
	6-31G*	-298.64140	3.256	3.256	180	431	286	762
	6-31+G*	-298.72442	3.286	3.286	180	397	262	754
	6-311G*	-298.91787	3.311	3.310	180	408	262	724
	6-311+G*	-298.96913	3.334	3.333	180	382	230	727
CISD	6-31G*	-298.56895	3.159	3.159	180	531	329	497
	6-31+G*	-298.63779	3.173	3.172	180	515	315	245
CASSCF	6-31G*	- ^b	-	-	-	-	-	-
	6-31+G*	-298.19004	4.375	2.873	180	146	160	632

^a*a*₀ ≈ 5.291 77 × 10⁻¹¹ m.
^bPoor convergence: see text for details.

extremely basis set dependent. Using the smallest, and almost certainly inadequate, 4-31G basis set, a symmetrical structure with a relatively large bond length was obtained. With an additional set of d polarization functions, an asymmetrical structure was obtained. This is essentially an F₂ molecule with an F⁻ at a relatively long intermolecular distance. This long and short bond structure persisted, as the basis set size was increased (cf. all SCF optimized geometries from reference [29], assuming a linear symmetric structure, gave one imaginary vibrational frequency). In contrast, at the MP2 level, a symmetrical, relatively long-bond structure was obtained consistently for all the basis sets used. The CISD optimized geometries were also similar to those of the MP2 calculations, although the latter yielded slightly shorter bond lengths. CASSCF calculations using the 6-31G* basis set failed to converge in the geometry optimization with convergence problems in the CASSCF energy iteration (probably due to the observed large changes in the occupancy numbers) at an unoptimized geometry. Nonetheless, the 6-31+G*/CASSCF calculation gave an optimized asymmetrical structure, similar to the corresponding RHF counterpart. The CASSCF calculations should be treated with some caution, since the active space is quite small and the basis set is limited. However, some qualitative insights on the bonding are apparent from the computed CASSCF wavefunction. Heard *et al.* [29] briefly reported results of single point MCSCF and MR-CI calculations on a C_{2v} structure. They obtained a coefficient of 0.93 for the reference configuration; 0.25 for the LUMO(σ_u⁺) ← HOMO(σ_g) double excitation; and 0.14 for a LUMO ← σ_u double excitation. A calculation was made here at the TZP+/CCSD geometry of reference 29 (linear, with bond lengths of 2.6817 *a*₀) using the 6-31+G* basis set. The result was similar to that of reference [29] with coefficients of 0.97, -0.19 and -0.10, respectively (note that the last two coefficients were quoted as positive in reference [29]). However, a single LUMO ← σ_u excitation also had a coefficient of 0.08. At the optimized (asymmetric) structure (6-31+G*/CASSCF) in this work the reference

configuration had a coefficient of 0.95, but the LUMO \leftarrow HOMO double excitation had a coefficient of less than 0.05. Also the LUMO $\leftarrow \sigma_u$ double excitation was more significant with a coefficient of -0.29 and two other minor contributions were a LUMO $\leftarrow \sigma_u$ single excitation (coefficient = 0.07) and a double excitation involving one σ_u and one HOMO electron both going to the LUMO (coefficient = -0.08). Hence the lower energy asymmetric structures seem to arise predominantly from the effect of the deeper excitation.

The only consistent geometrical parameter obtained by all the calculations discussed was the bond angle of 180° . It thus seems probable that F_3^- is linear.

The computed harmonic vibrational frequencies, obtained using different basis sets, as shown in table 1, are inconsistent at the HF level and, hence most probably unreliable. This suggests that the shapes of the HF energy surfaces are rather basis set dependent. The MP2 frequencies are, however, reasonably consistent with some observable trends against basis set variation. Both symmetrical modes went through a maximum with increased basis set size, while the antisymmetrical stretching mode decreased with increased basis set size.

Although only two basis sets were used (because numerical second derivative calculations were rather computationally expensive), the CISD ν_1 and ν_2 frequencies showed similar behaviour to the MP2 counterparts; the ν_3 frequency, however, was not well behaved. The computed CISD frequencies of both symmetrical modes were found to be significantly larger than the corresponding MP2 frequencies, while the opposite was observed for the antisymmetrical mode, indicating that the shapes of the energy surfaces obtained by two different correlation methods differed significantly. With such a large variation in the magnitude of the computed harmonic vibrational frequencies, as shown in table 1, it would be difficult to make any quantitative comparison with the available experimental values obtained from infrared matrix isolation studies, as any good agreement is quite likely to be fortuitous. Nonetheless, an attempt at doing so qualitatively will be given in a following subsection, together with the values for Cl_3^- .

The lowest triplet state of F_3^- has also been studied, using the 6-31G* and 6-31+G* basis sets. This is a $^3A'$ state, with two unpaired electrons in two different MOs, both of a' irreducible representation, in the C_s point group. The results are summarized in table 2. At the RHF level, the 6-31G* geometry optimization stopped with persistent failures in the search, though both the average and maximum gradients had converged, indicating that the surfaces were extremely flat. Nevertheless, the computed energy at the lowest energy point of this triplet state was considerably lower than that at the optimized geometry of the closed-shell singlet state (see table 1), suggesting that the triplet state was the ground state at the RHF level. A similar result was obtained from the 6-31+G*/RHF calculation although, for the triplet state, the 6-31+G*/RHF geometrical structure (near linear) was quite different from the 6-31G*/RHF structure (highly bent). UMP2 calculations using both basis sets, however, gave very similar geometries for the triplet state, which were highly bent (whether the starting geometry was near linear or highly bent). The calculated triplet energies were slightly higher than those of the closed-shell singlet state (see tables 1 and 2) at the UMP2 level using the respective basis sets, reversing the computed RHF ordering of the singlet and triplet states. The 6-31+G*/RHF linear structure of the triplet state is essentially a F^- with two F atoms at either end, as indicated by the calculated charge and spin densities. Because of the high charge density at the central F atom, the diffuse sp primitive functions were found to have

Table 2. $F_3 \dots (a')^1(a'')^1 {}^3A'$ optimized geometries and vibrational frequencies

Quantity	RHF	UMP2 ^a
	6-31G*	
r_1/a_0	3.980	3.480
r_2/a_0	4.005	3.481
θ/deg	110.5	105.5
Energy/ E_h	-298.10646 ^b	-298.59475 ^c
ν_1/cm^{-1}	—	531
ν_2/cm^{-1}	—	128
ν_3/cm^{-1}	—	529
Quantity	RHF	UMP2 ^a
	6-31+G*	
r_1/a_0	4.512	3.500
r_1/a_0	4.534	3.505
θ/deg	178	107
Energy/ E_h	-298.16816	-298.67221 ^d
ν_1/cm^{-1}	102	470
ν_2/cm^{-1}	18	124
ν_3/cm^{-1}	167	264

^a $\langle S^2 \rangle$ less than 2.03.^bSee text for details.^cPUMP2 energy = -298.59922 E_h .^dPUMP2 energy = -298.67710 E_h .

considerable contributions to the molecular wavefunction. This was the only occasion where the sp diffuse set was seen clearly to be important throughout the present study. For the bent UMP2 triplet structure, the charge density is distributed more evenly among the three F atoms, with slightly more negative charge at the terminal F atoms. Comparing the charge densities of the bent structure obtained at the RHF level with those at the UMP2 level using the 6-31+G* basis set, dynamic electron correlation seems to have moved the electron densities considerably, away from the central F atom, to the terminal F atoms. Note that, at the UMP2 level for both basis sets, the geometry, ν_1 and ν_2 values were reasonably consistent, whereas again ν_3 shows great variation.

CASSCF optimization was performed on the triplet state with a 6-31G* basis set, giving an optimized geometry very similar to that from the corresponding RHF calculation. From the computed CI coefficient of 0.9989 for the dominant RHF configuration, non-dynamic correlation clearly seems to be unimportant and a single-reference method should be sufficient for this state.

Attempts were made to search for other states: both RHF and CASSCF calculations using a 6-31G* basis set were carried out to locate the ${}^3A''$ state, with one unpaired electron in an a'' MO, and a $\dots (a')^1(a'')^1$ configuration. The RHF optimization showed similar behaviour to that of the ${}^3A'$ state, i.e. the gradients converged but the overall search failed. The CASSCF optimization also failed with convergence problems in the energy iteration procedure. The RHF energy at the lowest energy point was higher than that of the ${}^3A'$ state by about 0.03 E_h . It is probable that the 6-31G* basis set is inadequate for this electronic state. In order to confirm the ordering of the singlet/triplet states, single point configuration interaction calculations were also carried out. These were performed at the 6-31G*/CISD

Table 3. F_3^- Low-lying singlet and triplet states single-point CISD energies (6-31G*).

State	Configuration	E_{RHF}	E_{CISD}
$D_{\infty h}$ (using D_{2h} point group) ^a			
$^1\Sigma_g^+$	$..(\sigma_g)^2(\sigma_u)^0$	-298.04345	-298.56895 ^b
$^3\Sigma_u^+$	$..(\sigma_g)^1(\sigma_u)^1$	-298.057073	-298.55868
$^1\Sigma_u^+$	$..(\sigma_g)^1(\sigma_u)^1$	—	-298.26997 ^c
C_s ^d			
$^1A'$	$..(a')^2(a'')^0$	-298.00687	-298.54219 ^b
$^3A'$	$..(a')^1(a'')^1$	-298.09326	-298.55583
$^1A'$	$..(a')^1(a'')^1$	—	— ^e

^aEnergies calculated at the $^1\Sigma_g^+$ 6-31G*/CISD optimized geometry (see table 1).

^bIncluding the unoccupied σ_u MO in the reference configuration.

^cCalculated using the $^3\Sigma_u^+$ SCF MOs.

^dEnergies calculated at the $^3A'$ 6-31G*/UMP2 optimized geometry (see table 2).

^eWhen the $^3A'$ SCF MOs were used, this converged to a very mixed state with the $c_0 < 0.03$.

optimized geometry of the $^1\Sigma_g^+$ state and the 6-31G*/UMP2 optimized geometry of the $^3A'$ state, using the 6-31G* basis set. The calculated CISD energies are shown in table 3. At the RHF level, the triplet state was calculated to be more stable than the closed-shell singlet state at both chosen geometries. When dynamic correlation was included, the order changed, and the closed-shell singlet state became the more stable at the 6-31G*/CISD optimized geometry of the singlet state. However, at the 6-31G*/UMP2 optimized geometry of the triplet state, the CISD energy of the triplet state was calculated to be lower than that of the singlet state. This suggests that there would be a crossing between the singlet and triplet surfaces at the vicinity of the chosen geometries. Nevertheless, the singlet state at its optimized geometry still has the lowest energy among all calculated energies shown in table 3. It should be noted that the 6-31G*/UMP2 optimized geometry of the triplet state used will not be the same at the optimized geometry of the triplet state at the 6-31G*/CISD level. Consequently, the calculated CISD energy of the triplet state at this geometry is slightly higher than that calculated at the 6-31G*/CISD optimized geometry of the singlet state. The energy of the corresponding open-shell singlet state has also been calculated using the RHF MOs of the triplet state for the CI calculation at the two chosen geometries as discussed above, and was found to be considerably higher than the two states discussed above (see table 3). Summarizing, it seems reasonable to conclude that the closed-shell singlet state is the ground state of F_3^- , based on both the UMP2 and CISD calculations; however, the triplet state seems to be close in energy and should be considered in any further investigation.

3.2. Cl_3^-

A similar set of calculations was performed on Cl_3^- as those on F_3^- , although the number of basis sets used was slightly smaller, due to computational limitations. The results are shown in table 4. Again, as was the case for F_3^- , the RHF level of theory has yielded symmetrical structures with a small basis set, but asymmetrical structures

Table 4. Calculated energies, geometries and vibrational frequencies of the Cl₃⁻ molecule.^a

Method	Basis set	Energy/E _h	r ₁ /a ₀	r ₂ /a ₀	θ/deg	ν ₁ /cm ⁻¹	ν ₂ /cm ⁻¹	ν ₃ /cm ⁻¹
SCF	4-31G	-1377.01829	4.555	4.555	180	293	163	347
	4-31G*	-1377.08566	4.415	4.416	180	289	181	223
	6-31G*	-1378.46077	4.456	4.385	180	272	172	49
	6-31+G*	-1378.46855	5.057	3.992	180	364	145	99
MP2	4-31G	-1377.19149	4.653	4.651	180	257	144	383
	4-31G*	-1377.53395	4.441	4.442	180	265	166	334
	6-31G*	-1378.89807	4.454	4.454	180	248	156	294
	6-31+G*	-1378.91475	4.462	4.461	180	246	142	285
CISD	6-31G*	-1378.87172	4.436	4.437	180	260	163	203
	6-31+G*	-1378.88551	4.435	4.435	180	261	157	172
CASSCF	6-31G*	-1378.49126	4.536	4.536	180	—	—	—
	6-31+G*	-1378.49966	4.531	4.530	180	—	—	—

^aThe assignment of the frequencies given here for the 6-31G* basis set is the correct assignment for the ν₁; in reference [14], these were designated incorrectly. Also, the values for the 6-31G basis set in reference [14] should be: ν₁ = 279 cm⁻¹, ν₂ = 266 cm⁻¹ and ν₃ = 150 cm⁻¹.

with the larger basis sets. In fact, the energy surface is very flat since the symmetrical structure of Cl₃⁻ calculated with the 6-31G* basis set in reference [14] and the asymmetrical structure obtained here have almost identical energies (the final geometry will depend, to some extent, on the initial geometry and the tightness of the convergence criteria used). The inadequacy of the RHF description is indicated by the instability of the calculated ν₃ frequency, which varies from 350 cm⁻¹ to 50 cm⁻¹. This may be indicative of some sort of symmetry breaking in the wavefunction. Once the MP2 method was employed, however, then some consistency in the ν₃ values obtained was achieved, together with a consistent, symmetrical geometry. It would seem that, in the two cases of F₃⁻ and Cl₃⁻, dynamic correlation energy is stabilizing the potential energy surface. A similar conclusion could be drawn from the CISD calculations, which gave very similar calculated geometries and frequencies with the two basis sets used. The values for ν₁ and ν₂ are very similar from the CISD and the MP2 calculations, but the ν₃ frequency is significantly lower in the CISD case. On the whole, it seems that the calculated results of Cl₃⁻ are slightly more consistent than those of F₃⁻.

The CASSCF calculations for Cl₃⁻ have yielded reasonable results for the optimized geometries using both the 6-31G* and 6-31+G* basis sets, giving a symmetrical structure, similar to that from the MP2 and CISD calculations discussed above. This may suggest that for Cl₃⁻ the demands on accounting for both dynamic and non-dynamic electron correlation are only modest since, although the active space used in the CASSCF calculations is rather small as compared with the corresponding CISD calculations, they gave very similar optimized geometries. Comparing this with F₃⁻, where the CASSCF calculations gave an asymmetrical structure which was akin to that obtained at the RHF level, but different from the symmetrical structure obtained by both the MP2 and CISD calculations, it would seem that an accurate description of the energy surfaces of F₃⁻ is more demanding on the

Table 5. $Cl_3^- \dots (a')^1(a')^1 {}^3A'$ optimized geometries and vibrational frequencies.

Quantity	RHF	UMP2 ^a
6-31G*		
r_1/a_0	5.215	4.954
r_2/a_0	5.211	4.954
θ/deg	106	104
Energy/ E_h	-1378.44633	-1378.85426
ν_1/cm^{-1}	164	245
ν_2/cm^{-1}	43	67
ν_3/cm^{-1}	107	298
6-31+G*		
r_1/a_0	5.288	4.936
r_2/a_0	5.229	4.937
θ/deg	105	104
Energy/ E_h	-1378.45330	-1378.87134
ν_1/cm^{-1}	145	249
ν_2/cm^{-1}	40	68
ν_3/cm^{-1}	65	304

^a $\langle S^2 \rangle$ less than 2.03.

theoretical method used in accounting for both the dynamic and non-dynamic electron correlation than Cl_3^- .

The CASSCF wavefunction of Cl_3^- at the optimized geometry (6-31+G*/CASSCF) gave a reference configuration coefficient of 0.97. The LUMO \leftarrow HOMO double excitation had a coefficient of -0.20 while the LUMO $\leftarrow \sigma_u$ double excitation had a coefficient of -0.11; hence, the wavefunction is rather similar to that of F_3^- for a C_{2v} geometry (see [29] and above). Additionally, a LUMO $\leftarrow \sigma_u$ single excitation had a coefficient of -0.09. A CASSCF calculation was also performed at the 6-31+G*/SCF-optimized geometry (see table 4), and the results gave a reference configuration coefficient of 0.98. The LUMO \leftarrow HOMO double excitation coefficient had dropped to -0.07, while the LUMO $\leftarrow \sigma_u$ double excitation had increased to -0.15 (i.e. a similar effect of F_3^- on going from a symmetric to an asymmetric structure). The other minor contribution was the double excitation of one σ_u and one HOMO electron into the LUMO (coefficient = -0.07). The LUMO $\leftarrow \sigma_u$ single excitation had a coefficient of less than 0.05.

The lowest-lying triplet state of Cl_3^- (${}^3A'$) has also been studied using the 6-31G* and 6-31+G* basis sets at both the RHF and UMP2 level. The results are summarized in table 5. The optimized structures were found to be consistently highly bent. The energies of the triplet state at the respective levels of theory were calculated to be higher than those of the closed-shell singlet state in all cases. It seems therefore reasonably conclusive that the closed-shell singlet state is the ground state in Cl_3^- . Again, the RHF ν_3 frequencies are extremely low and vary greatly, and could be indicative of symmetry breaking; the UMP2 values behaved more consistently.

It might be worth noting that two other triplet states were also located in the UMP2 geometry optimizations. They were a ${}^3A'$ state with a $\dots (a'')^1(a'')^1$ configuration and a ${}^3A''$ state with a $\dots (a'')^1(a')^1$ configuration. The former was obtained using the 6-31G* basis set and had a highly bent geometrical structure. However, force constant calculations gave one imaginary frequency, indicating that the opti-

mized geometry corresponded to a first order saddle point. The calculated charge densities and molecular wavefunction show that it has a Cl^- in the centre with two terminal Cl atoms and their MOs are highly localized and essentially non-bonding. The latter triplet state was obtained using the 6-31+G* basis set, and it is near linear with one long and one short bond. It is essentially a Cl_2^- with a Cl atom at a relatively long intermolecular distance. Force constant calculations gave two imaginary frequencies, indicating that it is a second order saddle point.

3.3. Comparison with available experimental data

For F_3^- , Ault and Andrews [1,2] noted that the non-observance of the ν_1 frequency in the infrared, but its observance in the Raman, were indicative of a molecule with a centre of symmetry and, hence, linear. This is in general agreement with the results obtained here, and in other theoretical studies [19,24,25,27,29]. The experimental value for ν_1 is 461 cm^{-1} [2] which is in reasonable agreement with the values obtained when some dynamic electron correlation was accounted for. Interestingly, the experimental value is between the MP2 values of about 400 cm^{-1} and the CISD values of about 520 cm^{-1} . Three other theoretical studies have also reported values of 472 [24], 521 [27] and $440 \pm 10\text{ cm}^{-1}$ [29], in good agreement with the experimental value. These calculated values were, however, obtained from various numerical fitting procedures, sometimes with a small number of data points, in contrast to the values obtained here from analytical and numerical second derivative calculations at the MP2 and CISD level, respectively.

The MP2 values for ν_3 obtained here of about 750 cm^{-1} are, however, in poor agreement with the experimental value of 550 cm^{-1} [2], and can be compared with the TZP/ACCD value of 228 cm^{-1} obtained in reference [24]. The 228 cm^{-1} is surprisingly close to the CISD value (6-31+G* basis set) of 245 cm^{-1} obtained in this work; however, the CISD values in this work change greatly between the 6-31G* and the 6-31+G* basis sets. The best agreement between the calculated and observed values for the asymmetric stretching mode came from reference [29] (from a polynomial fitting and finite-displacement procedure), but only at a 'very large basis set'/CCSDT level (giving an extrapolated value of $535 \pm 20\text{ cm}^{-1}$). the DZ+sp*/MP2 value of 526 cm^{-1} from reference [27] also agreed reasonably well with the experimental value, although it was obtained by a fit to a parabola using a grid of points near the minimum. Clearly, extremely high level theoretical methods will have to be used to calculate reliably the vibrational frequencies of this species.

With Cl_3^- the experimental ν_1 (ν_2) values are about 270 cm^{-1} (165 cm^{-1}) [1,4,11,12], this may be compared with the calculated MP2 values of about 250 cm^{-1} (about 150 cm^{-1}) and the CISD values of about 260 cm^{-1} (about 160 cm^{-1}) obtained here. The experimental value of ν_3 is not too clear. Andrews and coworkers obtained 375 cm^{-1} [1,11,12], whereas Evans and Lo obtained a value of about 240 cm^{-1} [4]. The calculated MP2 values are about 300 cm^{-1} and the CISD values are about 190 cm^{-1} . Clearly, it would seem that again a higher level of theory will be needed (and possibly further experimental investigations) in order to obtain more reliable results, particularly for ν_3 .

No experimental data on the vibrational frequencies of the neutral species seem to be available.

Table 6. Calculated geometries of Cl_3 under different symmetry restraints at the RHF level.

Basis set	Energy/ E_h	r/a_0	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
C_{2v} symmetry assumed						
4-31G*	-1376.93879	4.183	148	322	139	1152
6-31G*	-1378.29729	4.143	148	323	140	1314
9s6p+d	-1378.39180	4.138	147	339	144	1472

Basis set	Energy/ E_h	r_1/a_0	r_2/a_0	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
C_s symmetry assumed							
4-31G*	-1376.94658	-	-	about 180	dissociated		
6-31G*	-1378.35733	7.646	3.761	176	18	13	599
9s6p+d	-1378.45006	7.679	3.786	180	19	13	596

3.4. Cl_3

It was part of the initial aim of this work to perform a similar set of calculations on the neutral species as with the anions. However, many difficulties were encountered, and a complete basis set variation was not possible. Difficulties included bad SCF convergence and failures in geometry search, probably due to extremely flat potential energy surfaces and/or inadequacy of the level of calculation employed in describing the system. One of the main conclusions that arose from a previous study was that Cl_3 demonstrated a minimum at a very asymmetric structure and this was suggested as being a possible van der Waals structure between a Cl atom and a Cl_2 molecule [14]. One of the aims of the present study was to see if this structure persisted at a higher level of theory, or was merely a computational artefact. Results from RHF calculations are shown in table 6; again asymmetric structures were obtained which were substantially lower in energy than the structures obtained when C_{2v} symmetry was assumed (although the structures obtained under C_{2v} symmetry were true minima). The fact that the structures and frequencies obtained with the 6-31G* and the 9s6p+d basis sets are so similar suggests that basis set effects seem to be unimportant at the RHF level. The first correlated level of theory tried was UMP2; however, the spin contamination in Cl_3 is extremely high ($\langle S^2 \rangle$ greater than 0.9) and so the results cannot be relied upon. CASSCF calculations, with a 6-31G* basis set, were then attempted as described above. It was intended to study the lowest-lying $^2A'$ and $^2A''$ states. However, convergence problems as mentioned were encountered for the latter state. Therefore, only results of the former state were obtained at the CASSCF level for Cl_3 . The structure obtained here was also asymmetric, with bond lengths of 3.906 a_0 and 7.449 a_0 but a bond angle of 103°. (Note, however, that when a slightly different exponent was used for the d polarization function (0.8 instead of 0.75) then a bond angle of 161° was obtained, although the bond lengths were almost identical.) When a 6-31+G* basis set was used, an almost identical optimized geometry was obtained.

3.5 F_3

With F_3 the situation was similar to the case of Cl_3 except that the calculations were somewhat more difficult to converge, and so the results obtained are somewhat

Table 7. Calculated geometries of F_3 under different symmetry restraints at the RHF level.

Basis set	Energy/ E_h	r/a_0	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
C _{2v} geometry assumed						
4-31G*	-297.64784	2.936	180	619	188	1805
6-31G*	-297.92130	2.937	180	614	187	1794

Basis set	Energy/ E_h	r_1/a_0	r_2/a_0	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
C _s geometry assumed							
4-31G*	-297.76501	5.186	2.544	159	82	32	1248
6-311G*	-298.12693	5.639	2.509	114	—	—	—

more sparse (see table 7). It is clear, however, that the asymmetric structures obtained for Cl_3 are also present for F_3 at the RHF level. Again, the similarity of the results obtained under C_{2v} symmetry for the 4-31G* and the 6-31G* basis sets suggest that basis set effects were small for this species at the RHF level. Attempts to obtain a C_s structure with other basis sets (6-31G*, 6-31+G* and 6-311+G*) failed due to very bad SCF convergence. UMP2 calculations were attempted, and again very high spin contamination ($\langle S^2 \rangle$ greater than 1.0) meant that these calculations were unreliable; also the geometry searches failed in a number of cases with the gradients far from the threshold.

CASSCF calculations were slightly more successful. Very similar, asymmetric structures were obtained for both the lowest $^2A'$ and $^2A''$ states with bond lengths of $2.80 a_0$ and $5.25 a_0$ with the 6-31G* basis set and $2.82 a_0$ and $5.90 a_0$ with the 6-31+G* basis set and almost identical bond angles of about 176° . Another structure (also a true minimum) was obtained for the $^2A'$ state at about 142° , but the geometry with a bond angle of about 176° was the one of lower energy. The former had almost exactly the same shorter bond length, with the other increasing by $0.01 a_0$ (with both basis sets). The $^2A''$ state was the lowest in energy and hence the ground state, but only by $2\text{--}5 \text{ cm}^{-1}$ at this level of theory, and the two minima on the excited $^2A'$ state surface differed by only $20\text{--}25 \text{ cm}^{-1}$. It would seem that there are a number of low-lying states very close in energy, and so quite a complex series of potential energy surfaces could be expected if a more detailed study of this molecule were to be performed.

Some calculations were also attempted briefly on the closely related ClF_2 radical, which has been studied previously under C_{2v} symmetry [37,38] and experimentally [39]. Similar results were obtained here as for Cl_3 and F_3 : UMP2 calculations were highly spin-contaminated ($\langle S^2 \rangle$ greater than 0.9); and asymmetric structures were obtained under C_s symmetry using RHF and CASSCF. Structures obtained under C_{2v} symmetry were again true minima, as in the cases of F_3 and Cl_3 , but of higher energy than the C_s structures at the RHF level.

4. Conclusions

In this work RHF, MP2, CISD and CASSCF calculations have been used to study the low lying states of F_3^- , Cl_3^- , F_3 and Cl_3 . From the calculated results, the following conclusions may be drawn. First, it seems that basis set size effects are

most critical at the RHF level. However, electron correlation is definitely important for the four species studied, and the RHF results are therefore not to be relied upon. Second, while dynamic electron correlation is in general important, it seems that, for the closed-shell singlet state of Cl_3^- , the comparatively small amount of dynamic electron correlation, as accounted for in the CASSCF calculations, is sufficient to give an optimized geometry which is very similar to both CISD and MP2 calculations (both of which would have accounted for any large amounts of dynamic electron correlation). Third, non-dynamic electron correlation is definitely important for the neutral trihalogens, but perhaps may not be too important for the X_3^- species. This may be seen from the similarity between the SCF and the CASSCF optimized geometries of the latter. However, it should also be noted that CCSD results from reference [29] suggested that F_3^- had very substantial multireference character, and a similar conclusion is reached here for both F_3^- and Cl_3^- . Finally, it is reasonably certain that the ground state of Cl_3^- is the closed-shell singlet state. For F_3^- this also seems to be the case, but the triplet state seems to be very close in energy. However, for the open-shell, neutral trihalogens, the ground state is far from certain. For F_3 , if the CASSCF C_s structure obtained is assumed to be correct, then the $^2A''$ state is the ground state, but it has been shown that there are a number of $^2A'$ states very close in energy. In addition, dynamic correlation energy contributions may change the geometrical and electronic structures of the trihalogen radicals considerably.

For the anions, the most consistent set of results, using different basis sets, was obtained for the MP2 calculations. The agreement between the calculated and the experimental vibrational frequencies was quite reasonable for Cl_3^- . However, for F_3^- , the experimental values lie between the MP2 and CISD values, in general.

If accurate potential energy curves are required in order to aid the interpretation of experimental data (such as the luminescence studies reported previously [13,14]) or to help in the search for further spectral features, then computational methods such as CASSCF followed by (MRD)CI methods, which account for both dynamic and non-dynamic correlation energy, would have to be used, particularly for the neutral trihalogen radicals. (However, this would probably have to be done in a point-by-point geometry search [40], and would clearly be computationally expensive and time consuming.) It should be noted that the asymmetric structures obtained for the neutral species are far from conclusive. A much more detailed study would be needed to determine the minimum energy structure of both F_3 and Cl_3 unequivocally.

Higher level calculations, as suggested above, are presently under consideration on all the species considered in this work, and it would perhaps be useful to study these species using the restricted, open-shell MP methods (ROMP) [41] (for the open-shell trihalogens), and the multireference perturbation method [42] in order to ascertain the importance of dynamic electron correlation at the single- and multi-reference levels respectively.

The authors thank Professor J. M. Dyke (Southampton) for useful discussions and for the use of some computer time at ULCC funded by the SERC. We also thank Dr J. G. Frey (Southampton) for introducing us to these interesting species. Some of the calculations were performed at the Technische Universität München, Germany where one of us (TGW) is funded under a Royal Society European Science Exchange Fellowship.

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