The Structure of CCI_5^- in the Gas Phase

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Abstract

The first experimental evidence of the structure of the CCl_5^- gas phase anion complex is presented in conjunction with results from high level theoretical calculations. The photoelectron spectrum of the system shows a single peak with a maximum at 4.22 eV. CCSD(T) detachment energies of two stable C_{3v} ion-molecule complexes of the form $Cl^- \cdots CCl_4$ were also determined. The first complex found features the Cl^- bound linearly in a $Cl^- \cdots Cl - C$ bonding arrangement, while the second, less stable minimum has the Cl^- positioned at the face of the CCl_4 molecule, midway between three chlorine atoms. The calculated detachment energy for the first complex was found to be in excellent agreement with experiment, allowing the structure of CCl_5^- in the gas phase to be postulated as a non-covalent $Cl^- \cdots CCl_4$ anion complex, with the Cl^- anion tethered by a typical halogen bond.

Graphical TOC Entry



The structure of a chloride ion bound to a CCl_4 molecule in the gas phase has not yet been the subject of experimental scrutiny. The existence of a stable form of the CCl_5^- anion was first proposed in 1966 by McDaniel and Deiters, who suggested either a $Cl_3C-Cl-Cl^$ bonding arrangement or a penta-coordinated carbon structure.¹ Later X-ray data of crystalline carbon tetrahalide complexes showed that one halide ion is bound to each apex of the core molecule,² while Raman studies found that in solution, the halide is positioned at the 'face' of the carbon tetrahalide, equally bound to three halogen atoms.^{3,4} Despite this, no structural information has been gained relative to the gas phase species; although several mass spectrometry experiments have confirmed its presence,⁵ with estimations for the heat of association as approximately -60 kJ mol⁻¹.⁶⁻⁸

The nomenclature ' CCl_5^- ' implies a stable, hypervalent, and pentahalogenated carbon species of D_{3h} symmetry, although theoretical studies have since confirmed that this purported structure is a saddle point linking two degenerate C_{3v} Cl⁻…CCl₄ complexes along an $S_N 2$ style pathway.⁹⁻¹² The stable complex in this form involves the halide at the face of the CCl₄ molecule. In addition, a second, more stable minimum has been predicted by theory, with the chloride bound linearly to a Cl atom of CCl₄ in what resembles a three-centred, fourelectron bonding motif.^{8,11-13} However, no experimental results to date have been able to elucidate the structure of CCl₅⁻, henceforth referred to as Cl⁻…CCl₄, in the gas phase.

The aim of this paper is to present a combination of theoretical and experimental results that support the existence of one stable isomer of $Cl^- \cdots CCl_4$ over another, and ascertain the gas phase structure of the anion complex for the first time. It will be shown through *ab initio* calculations that each isomer can be experimentally distinguished via their individual electron binding energies (*eBE*). Subsequent experimental data, in the form of mass spectrometry and photoelectron spectroscopy, will be used to present evidence as to the structure of the $Cl^- \cdots CCl_4$ anion complex in the gas phase.

Figure 1 displays the optimised geometries of the $Cl^- \cdots CCl_4$ isomers at the MP2/aug-ccpVQZ level of theory, using the aug-cc-pV(Q+d)Z basis set for $Cl^{.14,15}$ Vibrational analyses found all real frequencies for both conformers, while further details on structures and energetics can be found in the Supporting Information attachment, in addition to the optimised geometry of the D_{3h} saddle point mentioned previously. CCSD(T) energies were computed on these stable complexes with all values extrapolated to the complete basis set limit (CBS) using the W2w method unless stated otherwise.¹⁶



Figure 1: Optimised MP2/aug-cc-pVQZ (with the aug-cc-pV(Q+d)Z basis set for Cl) geometries of the C_{3v} Cl⁻…CCl₄ gas phase anion complexes.

The first C_{3v} chlorine-bound complex, to be referred to as Complex 1 as per Figure 1, features the Cl⁻ anion tethered linearly to one Cl of CCl₄ at a distance of 2.780 Å, and has a zeropoint corrected dissociation energy (D₀) of 46.7 kJ mol⁻¹. Carrion and Dewar¹³ first reported this structure with an accompanying Cl⁻…Cl distance of 2.13 Å and a heat of formation of 134 kJ mol⁻¹ using the MNDO method, prompting a call to label the ion as being covalently bound. Subsequent HF investigations by Kobychev et al.¹¹ as well as Vetter and Zülicke¹² found this distance to be 2.93 Å and 2.92 Å respectively, with dissociation energies of 43.1 kJ mol⁻¹ and 37.7 kJ mol⁻¹. Hiraoka et al. converged on this complex as well, reporting a B3LYP/6-31+G* distance of 2.82 Å and a QCISD(T) dissociation energy of 42.7 kJ mol⁻¹.⁸ With the excpetion of the MNDO calculations, we present the shortest Cl⁻…Cl distance reported for the anion complex, while all dissociation energies are in relative agreement.

In contrast, in the second C_{3v} structure of this work, labelled Complex 2, the Cl⁻ anion is equidistant to three Cl atoms of CCl_4 , 3.563 Å apart, and has a significantly lower D_0 value of 20.2 kJ mol⁻¹. The Cl⁻…C distance is 3.708 Å for our reported structure. This distance has been presented in the range from 3.78 Å to 4.15 Å in previous theoretical studies, with dissociation energies from 7.5 kJ mol⁻¹ to 19.7 kJ mol⁻¹.^{8–12} Additionally, Marchaj et al. most recently argued, upon taking into consideration thermal and entropic corrections, that the $Cl^- \cdots CCl_4$ geometry of Complex 2 is unlikely to be observed experimentally, especially at elevated temperatures.⁹ Based on the D_0 values of each complex presented in this work, it would be expected that Complex 1 is the more likely to be observed of the two isomers. Table 1 summarises the structural parameters of these systems, in addition to presenting the CCSD(T)/CBS vertical detachment energies (VDE) for each complex. These energies correspond to a simulation of the d calculat formatio the ${}^{2}P_{3}$ Table ometri while t

of the detachment of an electron associated with the Cl^- anion of each structure, with th
calculated geometries suggesting a non-covalent van der Waals interaction, as opposed to th
formation of a molecular anion. Raw photodetachment energies were split into transitions to
the ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ neutral states of Cl using the experimental spin-orbit coupling constant
Table 1: Summary of structural parameters of the $Cl^- \cdots CCl_4$ complexes. Ge ometrical information is from the relevant MP2 geometry optimised complex while the D_0 and VDE values were determined from $CCSD(T)/CBS$ energies See text for further information.

	$r_{\rm Cl^-\cdots Cl_1}$	$r_{\rm Cl^-\cdots Cl_2}$	D_0	VE	ЭE
	(Å)	(Å)	$(kJ mol^{-1})$	(eV)	V)
				$^{2}\mathrm{P}_{3/2}$	$^{2}\mathrm{P}_{1/2}$
Complex 1	2.780	5.426	46.7	4.23	4.34
Complex 2	5.500	3.563	20.2	3.72	3.83

Complex 1 has VDE values of 4.23 eV and 4.34 eV for transitions to the ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ states of Cl respectively, while these values are 3.72 eV and 3.83 eV for Complex 2. For

the case of Complex 2, the data is in good agreement with the 3.83 eV value presented by Marchaj et al.⁹ That the electron would be more tightly bound to the Cl⁻ of Complex 1 by more than 0.5 eV can be rationalised by the strength of anion D_0 values in relation to one another.

Needless to say, the large difference in energy between the two detachment energies suggests that the presence of each conformer can be determined through experimental photoelectron spectroscopy. It is also noted at this point, that VDEs produced from theory to predict or rationalise experimental photoelectron spectra have been used previously with great success, including those at the CCSD(T) level of theory.^{17–19}



Figure 2: A mass spectrum over the range of 140-200 m/z from a gas mixture of CCl_4 , CH_3CH_2OH , and Ar. The cluster of peaks from 187 m/z to 193 m/z corresponds to the presence of the $Cl^- \cdots CCl_4$ gas phase anion complex.

Shown in Figure 2 is a mass spectrum resulting from a gas mixture consisting of CCl_4 , CH_3CH_2OH , and made up to 400 kPa with Ar. The ethanol added to the mixture was in an attempt to characterise the $Cl^- \cdots CH_3CH_2OH$ system, although has no relevance to the investigation at hand, with the presence of the $Cl^- \cdots CCl_4$ anion complex detected in unrelated Cl^- based experiments. Cl^- anions were produced via a process of dissociative attachment to CCl_4 , with electrons provided by a hot rhenium filament. The major characterising feature from the m/z region between 140 and 200 is a series of four peaks at m/z values of 187, 189,

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191, and 193, highly indicative of the touted $Cl^- \cdots Ccl_4$ system. The relative abundance of each mass peak is in good agreement with those that have been previously reported,⁷ and follows from the natural abundance of the chlorine isotopes. Also present in the mass spectrum are complexes resulting from a residual amount of CH_3I of a previous experiment; notably $I^- \cdots H_2O$ at 145 m/z, $I^- \cdots Ar$ at 167 m/z, and $Cl^- \cdots CH_3I$ at 177 and 179 m/z. Photoelectron spectra were collected for the bare Cl^{-} and l^{-} ions for calibration, while the spectrum of the $Cl^- \cdots CCl_4$ system was recorded using the largest mass peak occurring at 189 m/z. This photoelectron spectrum is reported in Figure 3, characterised by a single peak with a maximum at 4.22 eV, the experimentally determined eBE. The 0.18 eV spread in photoelectron energy of this peak, resulting from the mass of the complex and a beam energy of 1500 eV,²⁰ in turn leading to a full width half maximum of 0.07 eV, obscures any possible distinction of a perturbed ${}^{2}P_{1/2}$ Cl spin-orbit state, as would be expected for a Cl⁻ anion core interacting non-covalently with an adduct molecule. However, there is a small should occurring at slightly higher eBE which could amount to a small protrusion of the ${}^{2}P_{1/2}$ neutral state, or even a vibrational progression, as has been observed for similar systems.^{21,22}

The general shape of the novel peak is consistent with that of the bare Cl⁻ photoelectron spectrum shifted approximately 0.58 eV to higher eBE, as the maximum of the bare halide photoelectron peak was measured at 3.64 eV. The magnitude of this electron stabilisation energy (E_{stab}) is usually indicative of the strength of the van der Waals interaction between the halide anion and complexing molecule. For example, the Cl⁻…N₂ ion-induced dipole complex experiences an E_{stab} of 0.11 eV,²³ whereas this figure is 0.76 eV for the ion-dipole Cl⁻…H₂O gas phase complex.²⁴ The E_{stab} of 0.58 eV observed in the current experiment is therefore indicative that the Cl⁻…CCl₄ complex is bound rather tightly, likely through the halogen bond motif of Complex 1, which is debated to comprise of purely coulombic terms, being electrostatic and polarisation,^{25,26} in addition to some contribution resulting from charge transfer.^{27,28}



Figure 3: Photoelectron spectrum of the $Cl^- \cdots CCl_4$ gas-phase anion complex from 0 to 4.661 eV. The maximum of the photoelectron peak occurs at 4.22 eV. The theoretical VDEs to a neutral ${}^2P_{3/2}$ state of Complex 1 (dashed line) and Complex 2 (dotted line) are overlayed for comparison.

Figure 3 also shows the comparison between the experimental photoelectron spectrum (black line) and the ${}^{2}P_{3/2}$ VDE predictions of Complex 1 (dashed line) and Complex 2 (dotted line). It is readily apparent that the high level predictions for Complex 1 are in excellent agreement with the experimentally determined eBE. Therefore, the results we present here are indicative that the structure of $Cl^- \cdots CCl_4$ in the gas phase is that of a chloride ion forming a van der Waals complex with the CCl_4 molecule, bound linearly to a Cl atom as per the depiction of Complex 1 in Figure 1.

Additionally, there appears to be no indication that there is any photodetachment peak resulting from the presence of Complex 2. There is a small portion of noise between 3.50-4.00 eV in Figure 3, however this is likely due to background subtraction becoming more pronounced in a region where the applied Jacobi transform is beginning to show an effect. This transform involves multiplying the photoelectron intensities by their time-of-flight cubed, t^3 , in order to move from time-dependent bins to energy-dependent. Therefore, we can say with confidence that little to none of the experimental $\text{Cl}^-\cdots\text{CCl}_4$ mass peak results from the existence of Complex 2, under the present experimental conditions.

The only caveat to the experimental results is that the ${}^{2}P_{1/2}$ neutral state of Cl is obscured; a feature that would be observable at higher resolution. The distinguishing of both neutral states of Cl would allow the conclusion to be made, beyond reasonable doubt, that the proposed CCl₅⁻ system is best described by a chloride ion adducting non-covalently to CCl₄, although the combination of theory and experiment presented here does support the existence of a Cl⁻…CCl₄ van der Waals complex.

To complement the experimental results, we have undertaken two theoretical approaches to determine the bond index of the $Cl^- \cdots Cl$ bond in Complex 1. The first involves the methodology set out by Oliveira et al., using calculated local stretching force constants to determine a bond strength order (BSO).²⁹ This method yields a BSO of 0.219 for the $Cl^- \cdots Cl$ bond, and 1.006 for the $Cl^- C$ bond along the axis of the Cl^- adduct. Interestingly, this would correspond to a percentage of three-centred four-electron bonding of 22%. The BSO of the $Cl^- \cdots Cl$ bond strength hierarchy put forward by Oliveira et al.²⁹ As a note, the force constants used in this calculation can be found along with vibrational modes in the Supporting Information.

The second method utilised the Roby-Gould bond index program using the Tonto computational chemistry package.³⁰ Further information about this method has been reported.^{31–33} The overall $Cl^- \cdots Cl$ bond index was found to be 0.269 for the geometry of Complex 1, in what is reasonable agreement with the index predicted through stretching force constants. These results are consistent with the conclusion that the $Cl^- \cdots CCl_4$ complex studied experimentally in this work is likely to consist of a chloride ion bound non-covalently to a CCl_4 molecule in a $Cl^- \cdots Cl - C$ bonding arrangement.

In summary, the first experimental evidence as to the structure of the CCl_5^- , or rather, the $Cl^-\cdots CCl_4$ gas phase anion species has been presented. Mass spectrometry experiments were used to confirm the production of the system, before characterisation with photoelectron spectroscopy. The photoelectron spectrum features a single peak with a maximum at 4.22 eV, found to be in excellent agreement with the CCSD(T)/CBS predicted VDE of Complex 1 of Figure 1, which was determined to be 4.23 eV and 4.34 eV for detachments to the neutral ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ states of Cl respectively.

The structure of this C_{3v} complex has the halide appended non-covalently to a singular Cl of CCl_4 in what resembles a typical halogen bond, and is bound by 46.7 kJ mol⁻¹. Based on a combination of the theoretical and experimental results, we assign this complex as being the form of $Cl^- \cdots CCl_4$ in the gas phase.

A second stable C_{3v} complex was also found by *ab initio* calculations, with the Cl⁻ anion postioned at the face of the CCl₄ molecule, and this is thought to be a more purely electrostatically driven interaction. Complex 2 was found to have a dissociation energy of 20.2 kJ mol⁻¹, less than half that of Complex 1. Rationalising the theoretical VDE predictions in relation to the experiment, there is no indication that Complex 2 was observed experimentally.

The experimental data outlined in this paper was recorded using a home built time of flight mass spectrometer coupled to a photoelectron spectrometer. The design of the mass spectrometer is owed to Wiley and McLaren,³⁴ while the magnetic-bottleneck feature of the photoelectron spectrometer is derived from Cheshnovsky.²⁰ Further information on the experimental design has been reported.³⁵

The fourth harmonic of a Nd:YAG laser (Spectra Physics Quanta Ray Pro) was used to generate the 4.661 eV photons used for this experiment. Upon photodetachment, electron counts were recorded as per their time of flight, before conversion to kinetic energy and subsequently eBE based on the energy of the input photon. Photoelectron spectra were recorded over 10 000 shots, before averaging, as well as the application of a Jacobi transform.

All calculations were carried out using the Gaussian 09 program,³⁶ unless stated otherwise. As mentioned, geometries and frequencies were determined at the MP2/aug-cc-PVQZ level of theory, with the aug-cc-pV(Q+d)Z basis set used for Cl.^{14,15} Very tight convergence criteria (1 x $10^{-8} E_h a_0^{-1}$) were applied during optimisations. Single point CCSD(T) energies on both the stable anion minima and the neutral vertically-detached counterparts were determined up to the quality of aug-cc-pV5Z/aug-cc-pV(5+d)Z before CBS extrapolation. Further details on the results of this process are outlined in the Supporting Information.

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Supporting Information Available

The following files are available free of charge.

• SuppInfo.pdf: Energetics, vibrational modes, and cartesian coordinates of the stable C_{3v} complexes outlined in this work, in addition to the D_{3h} saddle point.

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49x44mm (600 x 600 DPI)





Optimised MP2/aug-cc-pVQZ (with the aug-cc-pV(Q+d)Z basis set for CI) geometries of the C_{3v} Cl⁻···CCl₄ gas phase anion complexes.

40x18mm (600 x 600 DPI)



A mass spectrum over the range of 140-200 m/z from a gas mixture of CCl₄, CH₃CH₂OH, and Ar. The cluster of peaks from 187 m/z to 193 m/z corresponds to the presence of the Cl⁻···CCl₄ gas phase anion complex.

83x64mm (600 x 600 DPI)



Photoelectron spectrum of the Cl⁻···CCl₄ gas-phase anion complex from 0 to 4.661 eV . The maximum of the photoelectron peak occurs at 4.22 eV. The theoretical VDEs to a neutral ${}^{2}P_{3/2}$ state of Complex 1 (dashed line) and Complex 2 (dotted line) are overlayed for comparison.

83x83mm (600 x 600 DPI)

SUPPORTING INFORMATIONL

The supporting information presented here comprises results of *ab initio* calculations performed on $Cl^- \cdots CCl_4$ gas phase anion complexes, and the CCl_5^- transition state . Included are the energies, vibrational data, and cartesian coordinates predicted at the MP2 and CCSD(T) levels of theory, with aug-cc-pVTZ, QZ, and 5Z basis sets. The aug-cc-pV(X+d)Z basis sets were used for chlorine. Collectively, these basis sets will be referred to as AVXZ.

1 Energetics

		E _{(CCSD(T))}	VDE	Experimental SO*	Split	Lit. ${}^{2}P_{3/2}^{\dagger}$	Shift [‡]
		$[E_h]$	[eV]	[eV]	[eV]	[eV]	[eV]
Cl ⁻ Cl	AVTZ	-459.8066265 -459.6778578	3.504		3.468 3.577		+0.145
	AVQZ	-459.6958913 -459.8283951	3.606		3.570 3.679		+0.043
	AV5Z	-459.7013126 -459.8348346	3.633		3.597 3.706		+0.016
	CBS	-459.7066880 -459.8412328	3.661	-0.036 +0.073	3.625 3.734	3.613	-0.012

Table S1: Energies of the bare chloride anion and chlorine radical determined from CCSD(T) calculations.

* Values from http://www.nist.gov/pml/data/handbook/index.cfm

† Values from http://webbook.nist.gov

‡ Shift refers to the difference between the predicted and literature Electron Detachment Energy

Table S2: Energies of the C_{3v} halogen-appended $Cl^- \cdots CCl_4$ gas phase anion complex and neutral counterpart predicted from CCSD(T) calculations.

		Anion _{(CCSD(T))}	Neutral _{(CCSD(T))}	zpe	De	${\mathsf D_0}^\dagger$	VDE^{\dagger}
		$[E_h]$	$[E_h]$	$[kJ mol^{-1}]$	$[kJ mol^{-1}]$	$[kJ mol^{-1}]$	[eV]
$Cl^-\cdots CCl_4$	AVTZ	-2336.7998247	-2336.6479978				
	AVQZ	-2336.9106662	-2336.7549268	26.7*			
	AV5Z	-2336.9447580	-2336.7879148				
	CBS	-2336.9785121	-2336.8205701		47.5	46.7	4.23 4.34

* MP2/AVQZ value

† Determined using CCSD(T)/CBS energies and MP2/AVQZ zpe

Table S3: Energies of the C_{3v} Cl⁻…CCl₄ gas phase anion complex, featuring the halide at the face of the CCl₄ molecule, and neutral counterpart predicted from CCSD(T) calculations.

		Anion _{(CCSD(T))}	Neutral _{(CCSD(T))}	zpe	De	${\rm D_0}^\dagger$	VDE^{\dagger}
		$[E_h]$	$[E_h]$	$[kJ mol^{-1}]$	$[kJ mol^{-1}]$	$[kJ mol^{-1}]$	[eV]
$Cl^- \cdots CCl_4$	AVTZ	-2336.7899093	-2336.6539300				
	AVQZ	-2336.9006398	-2336.7607232	26.6*			
	AV5Z	-2336.9347036	-2336.7937173				
	CBS	-2336.9684218	-2336.8296220		21.0	20.2	3.72 3.83

* MP2/AVQZ value

† Determined using CCSD(T)/CBS energies and MP2/AVQZ zpe

2 Vibrational Data

Mode	Symmetry	Frequency	Force constant
ω_1	A_1	786	4.749*
ω_2	E	775	4.609
ω_3	E	775	4.609
ω_4	A_1	448	4.128
ω_5	E	326	2.048
ω_6	E	326	2.048
ω_7	A_1	309	1.799
ω_8	E	226	1.053
ω_9	E	226	1.053
ω_{10}	A_1	125	0.317*
ω_{11}	E	68	0.093
ω_{12}	E	68	0.093
zpe	26.7		

Table S4: Vibrational frequencies for the halogen-appended $Cl^- \cdots CCl_4$ gas phase anion complex from MP2/AVQZ calculations. Frequencies in cm⁻¹, zero point energies (zpe) in kJ mol⁻¹, force constants in mDyne Å⁻¹.

*Respective Cl-C and Cl⁻…Cl local stretching force constants used in main text to determine an approximate bond strength order.

Table S5: Vibrational frequencies for the Cl⁻…CCl₄ gas phase anion complex, featuring the halide at the face of the CCl₄ molecule, from MP2/AVQZ calculations. Frequencies in cm⁻¹, zero point energies (zpe) in kJ mol⁻¹, force constants in mDyne Å⁻¹.

Mode	Symmetry	Frequency	Force constant
ω_1	Е	826	5.297
ω_2	Е	826	5.297
ω_3	A_1	753	4.394
ω_4	A_1	475	4.584
ω_5	Е	323	1.931
ω_6	Е	323	1.931
ω_7	A_1	313	1.867
ω_8	Е	221	1.004
ω_9	Е	221	1.004
ω_{10}	A_1	77	0.117
ω_{11}	Е	48	0.046
ω_{12}	Е	48	0.046
zpe	26.6		

Mode	Symmetry	Frequency	Force constant
ω_1	E'	919	6.562
ω_2	E'	919	6.562
ω_3	A_1'	460	4.365
ω_4	$A_2^{\prime\prime}$	302	1.724
ω_5	E'	289	1.535
ω_6	E'	289	1.535
ω_7	E''	230	1.086
ω_8	E''	230	1.086
ω_9	E'	134	0.363
ω_{10}	E'	134	0.363
ω_{11}	A_1'	123	0.314
ω_{12}	$A_2^{\prime\prime}$	-557	2.367
zpe	24.1		

Table S6: Vibrational frequencies for the CCl_5^- transition state from MP2/AVQZ calculations. Frequencies in cm⁻¹, zero point energies (zpe) in kJ mol⁻¹, force constants in mDyne Å⁻¹.

3 Cartesian Coordinates

		Х	у	Z	
	С	0.000000	0.000000	-0.817022	
	Cl	0.000000	1.660488	-1.452849	
C_{3v}	Cl	0.000000	0.000000	0.933545	
	Cl	1.438025	-0.830244	-1.452849	
	Cl	-1.438025	-0.830244	-1.452849	
	Cl	0.000000	0.000000	3.713364	

Table S7: Cartesian coordinates of the geometry of the halogen-appended $Cl^- \cdots CCl_4$ gas phase anion complex optimised at MP2/AVQZ, in Å.

Table S8: Cartesian coordinates of the geometry of the $Cl^- \cdots CCl_4$ gas phase anion complex optimised at MP2/AVQZ, in Å, featuring the halide at the face of the CCl_4 molecule.

		Х	У	Z	
	С	0.000000	0.000000	-0.668872	
	Cl	0.000000	0.000000	-2.461208	
C_{3v}	Cl	0.000000	1.659347	-0.113911	
	Cl	1.437036	-0.829673	-0.113911	
	Cl	-1.437036	-0.829673	-0.113911	
	Cl	0.000000	0.000000	3.039013	

Table S9: Cartesian coordinates of the geometry of the CCl₅⁻ transition state optimised at MP2/AVQZ, in Å.

		X	У	Z	
	С	0.000000	0.000000	0.000000	
	Cl	0.000000	1.713893	0.000000	
D_{3h}	Cl	-1.484275	-0.856946	0.000000	
	Cl	0.000000	0.000000	2.430953	
	Cl	1.484275	-0.856946	0.000000	
	Cl	0.000000	0.000000	-2.430953	