Cl^- from some chloroalkanes (photochemical pathways and structures)

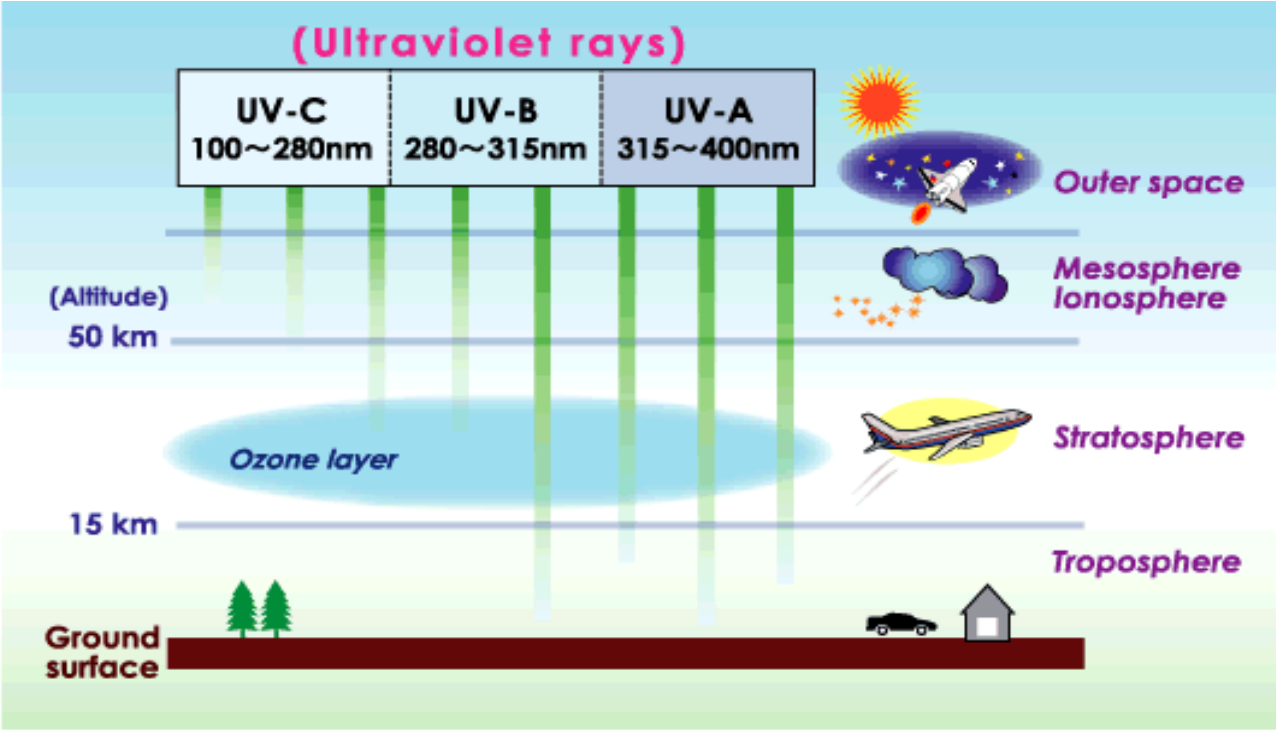
COLUMBUS
IN JOÃO PESSOA
November 07-09, 2019
João Pessoa - Paraíba

ONDE O SOL
NASCE PRIMEIRO!

LMRQ
Laboratório de Modelagem Molecular de Reações Químicas

Introduction

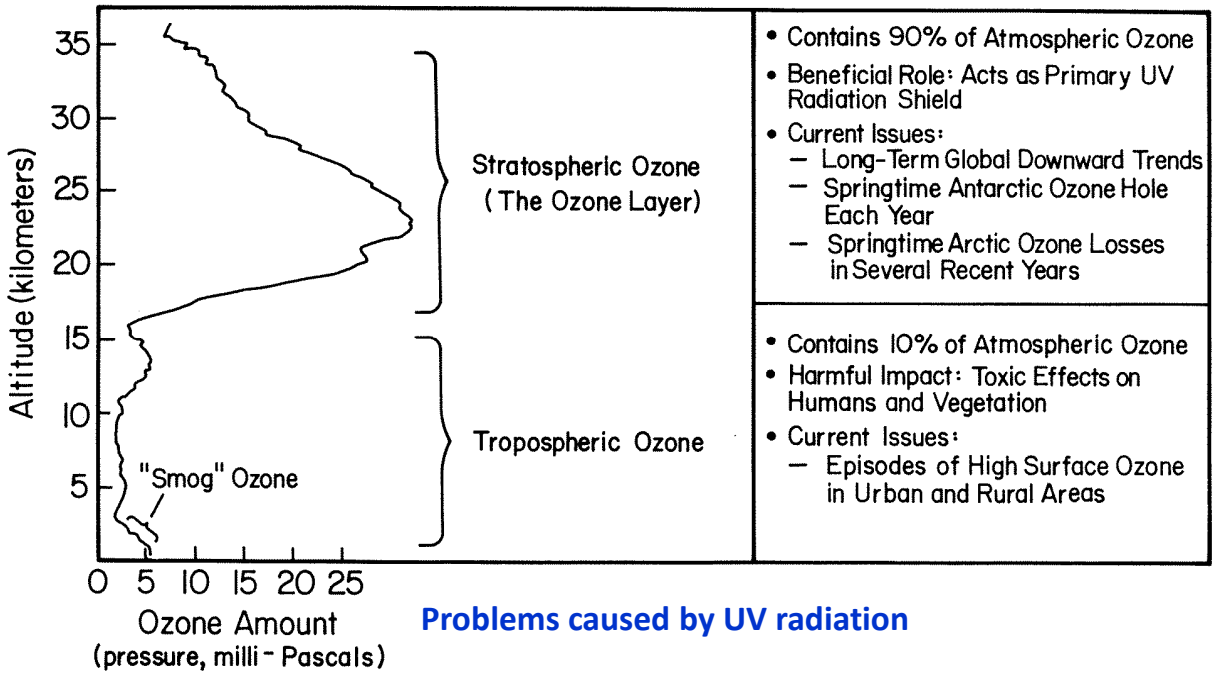
Ozone layer and the CFCs



Credit:Center for Global Environmental Research, National Institute for Environmental Studies Japan

Introduction

Ozone layer and the CFCs



Problems caused by UV radiation

Introduction

Ozone layer and the CFCs

Industrial and domestic use of CFCs

1929: Former gases used in refrigerators were (and still are!) toxic : NH_3, SO_2, etc.

Introduction

Ozone layer and the CFCs

Industrial and domestic use of CFCs

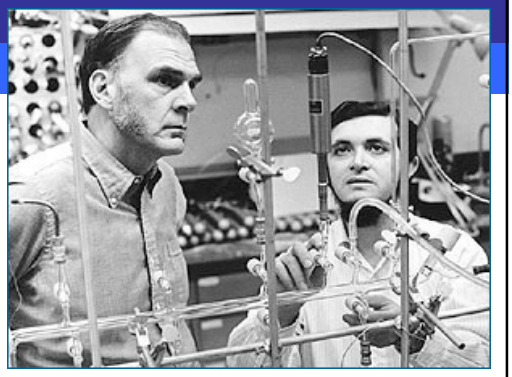
1928-29: Thomas Midgley "invented" CFC-12 (CF_2Cl_2)

Advantages: non-toxic, non-flammable, easily stocked , relatively cheap production, stable, versatile (refrigeration, solvent, etc...)

Freon: The "safe" gas (3 de novembro de 1934)

Introduction

Ozone layer and the CFCs



First studies concerning the effect of CFCs

1973: James Lovelock detected CFC-11 ($CFCl_3$) in the atmosphere.[1]

1974: Rowland e Molina suggested that CFC´s, when reach stratosphere, absorb solar radiation, releasing atomic Cl, which deplets O_3 catalitically.[2]

$$\mathbf{CFCl_3} + h\nu \rightarrow CFCl_2 + Cl \quad \text{(CFC-11)}$$

$$\mathbf{CF_2Cl_2} + h\nu \rightarrow CF_2Cl + Cl \quad \text{(CFC-12)}$$

185 nm (6.7 eV) < λ < 200nm (6.20 eV) (UVC)

→Highest effect around 23 – 35 km .

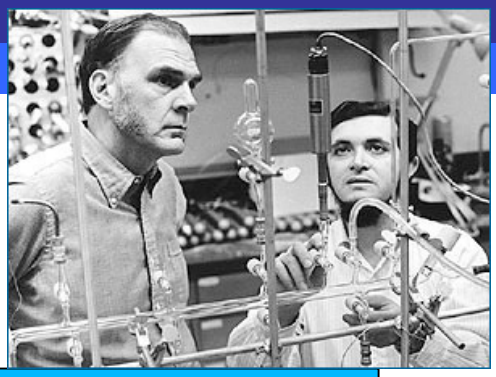
[1] *Nature,* 1973(241) 194-196; [2] *Nature*, 1974(249), 810-812

Introduction

Ozone layer and the CFCs

First studies concerning the effect of CFCs

Molina group used previous knowledge about UV absorption spectrum, by J. Doucet *et. al.* (cited in *Nature*, 1974(249), 810-812.)



Vacuum ultraviolet and photoelectron spectra of fluorochloro derivatives of methane

J. Doucet, P. Sauvageau, and C. Sandorfy

nσ* !

Citation: The Journal of Chemical Physics **58**, 3708 (1973); doi: 10.1063/1.1679722

The photoelectron and vacuum ultraviolet absorption spectra (200–120 nm) of CF_3Cl, CF_3Br, CF_2HCl, CFH_2Cl, $CFHCl_2$, CF_2Cl_2, and $CFCl_3$ are reported and discussed. The lowest ionization potentials belong to the chlorine or bromine lone pair orbitals, the next highest ones to the bonding orbitals of mainly C–Cl or C–Br character. In the absorption spectra the lowest freuqency bands are due to weak valence-shell type transitions. At higher freuqencies we find much stronger Rydberg type bands related to the first ionization potential. All absorption bands up to 84 000 cm^{-1} depart from chlorine or bromine lone pair orbitals. Some of the bands exhibit vibrational fine structure. An increase in the number of the fluorine atoms causes a shift to either higher or lower energies of the ionization potentials belonging to orbitals of mainly C–H or C–Cl character according to the cases while the lone pair ionization potentials and the absorption spectra shift to higher energies in all cases.

Introduction

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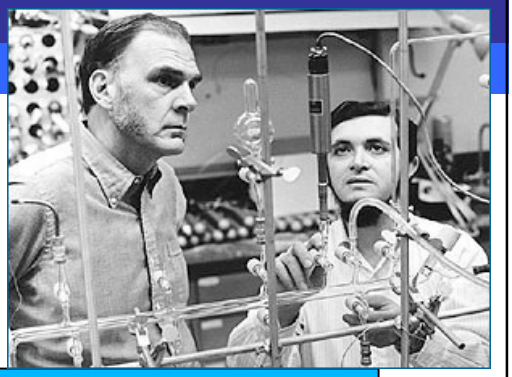

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31, 21, 12, and 11 in the above order. The photochemical reactions of these compounds could not be understood without a knowledge of their spectra. They might be important from the point of view of their ecology.

Introduction

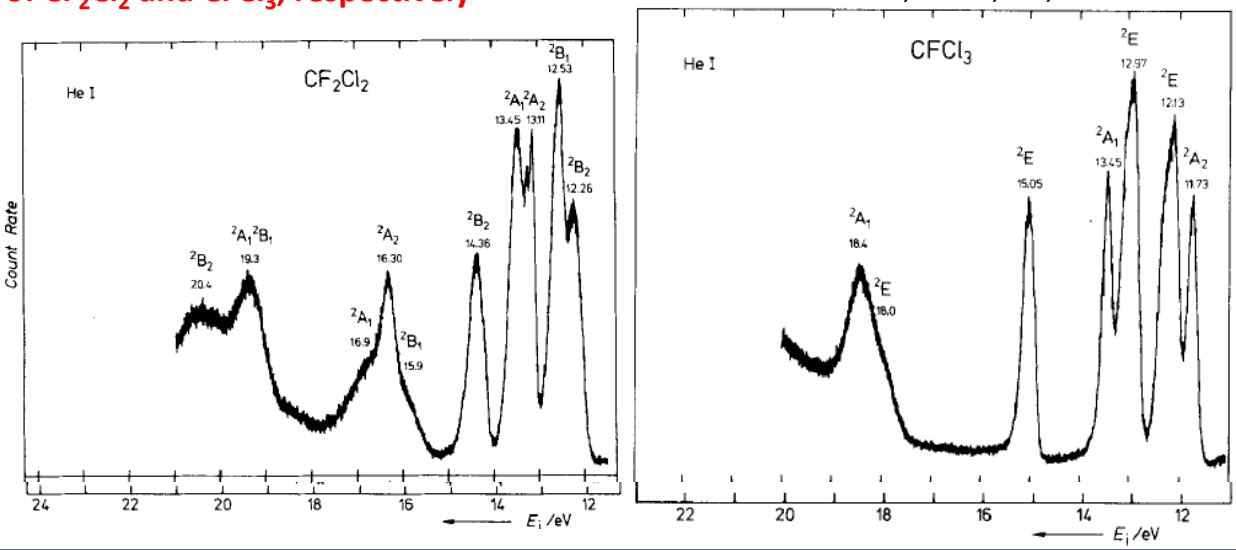
Ozone layer and the CFCs

First studies concerning the effect of CFCs

Molina group used previous knowledge about UV absorption spectrum, by J. Doucet *et. al.* (cited in *Nature*, 1974(249), 810-812.)

Four and six different bands have been identified in the photoelectron spectra of CF_2Cl_2 and $CFCl_3$, respectively

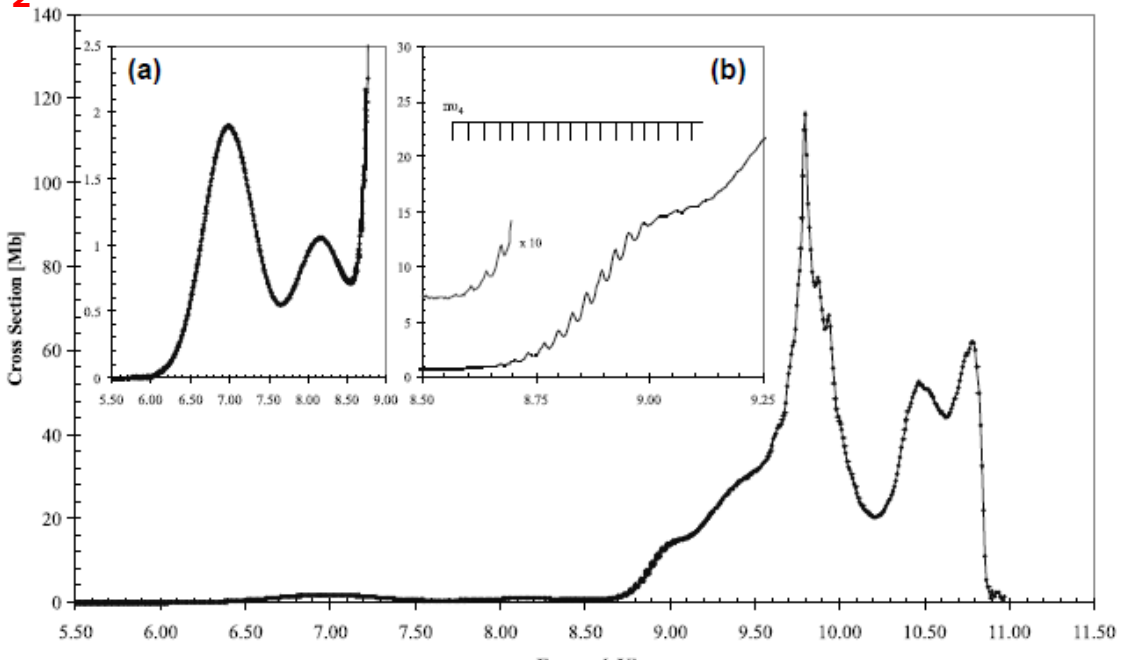
T. Cvitaš et. al. JCP, 1977, 67, 2687.



Introduction

Ozone layer and the CFCs

CF_2Cl_2

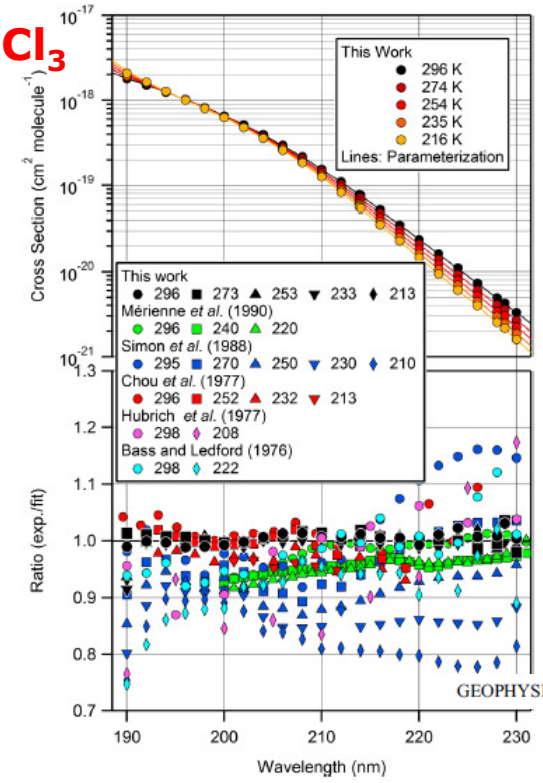


P. Limão Vieira et al. / Chemical Physics Letters 364 (2002) 535–541

Introduction

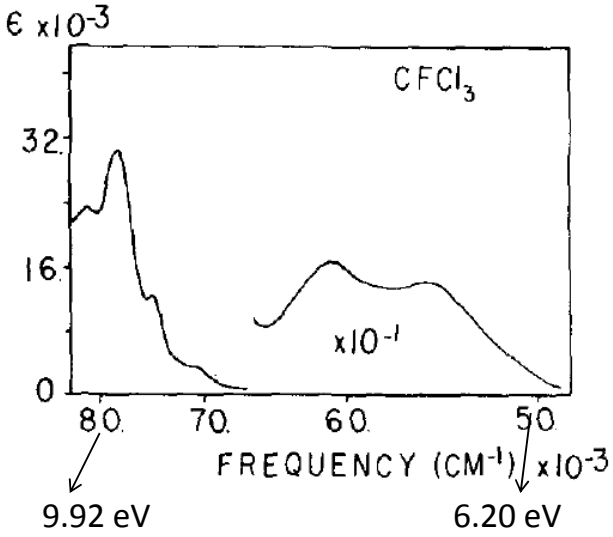
Ozone layer and the CFCs

$CFCl_3$



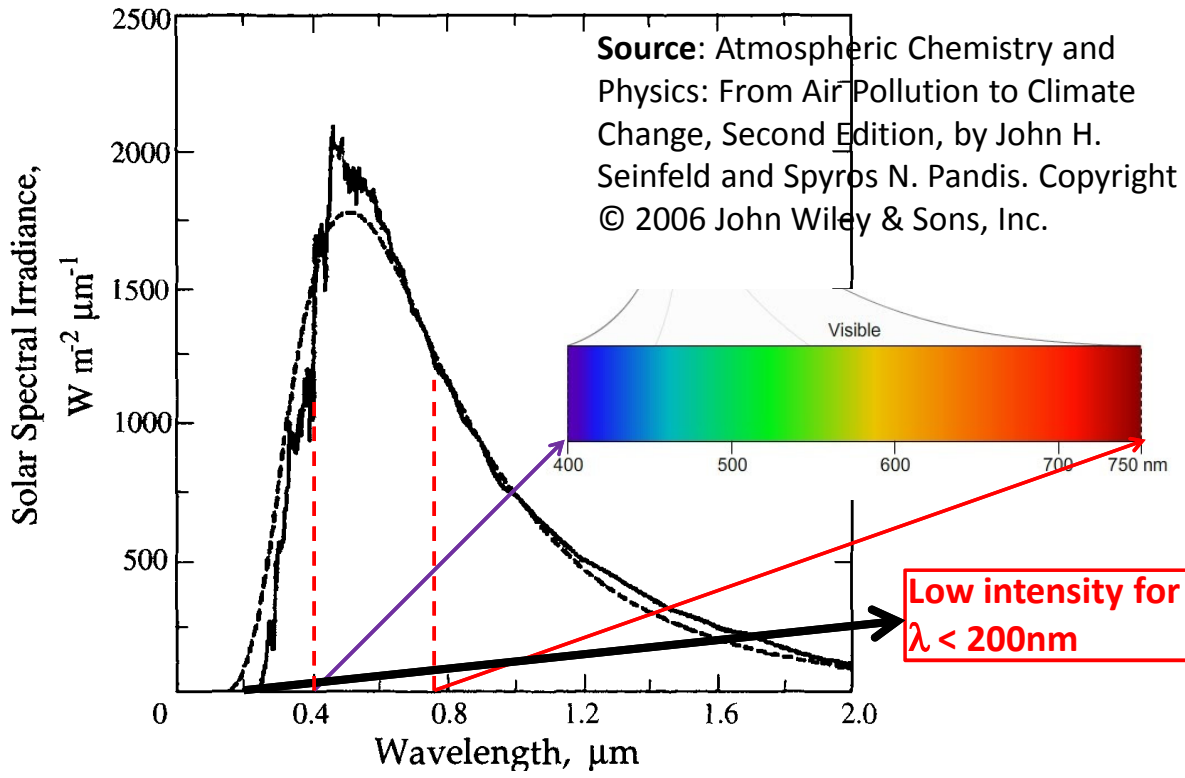
J. Doucet et. al.

The Journal of Chemical Physics **58**, 3708 (1973);



GEOPHYSICAL RESEARCH LETTERS, VOL. 40, 4772–4776, doi:10.1002/grl.50915, 2013

→Solar radiation reaching the atmosphere



Source: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Second Edition, by John H. Seinfeld and Spyros N. Pandis. Copyright © 2006 John Wiley & Sons, Inc.

→UV radiation

⇒**However, one still has a significative intensity in the region: 200 nm < λ < 400 nm**

→**UV: between 10 e 400 nm**

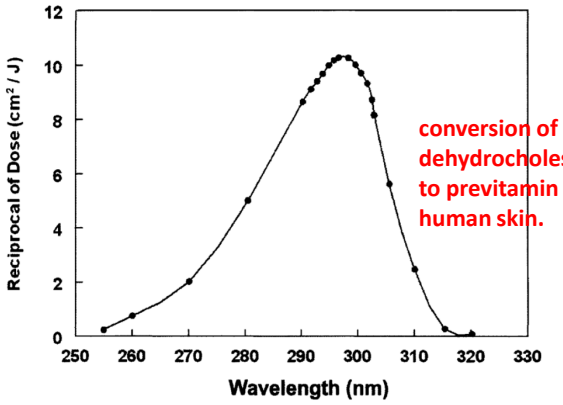
UVA: 315 nm < λ < 400 nm

UVB: 280 nm < λ < 315 nm

UVC: 100 nm < λ < 280 nm

This is more harmful to the cells ! (affects DNA)

⇒**There is also a "good" effect (270 nm < λ < 310nm) is important to yield previtamin D_3.**



conversion of 7-dehydrocholesterol to previtamin D_3 in human skin.

Source: M. Wackera & M. F. Holick, *Sunlight and Vitamin D*, Dermato-Endocrinology 5:1, 51–108; January/February/March 2013

Introduction

Ozone layer and the CFCs

→**Cl is highly reactive with respect to O_3, leading rapidly to O_3 depletion, involving ClO radical:**

$$\mathbf{Cl} + O_3 \rightarrow ClO + O_2$$
$$\mathbf{Cl}O + O \rightarrow \mathbf{Cl} + O_2$$

→**Net reaction:** $\mathbf{O_3 + O \rightarrow O_2 + O_2}$

→**One single Cl atom** can destroy ~ 100000 O_3 molecules[3] !!

[3]International Journal of Environmental Science and Development, Vol.2, No.1, February 2011

Introduction

Ozone layer and the CFCs

"Without a protective ozone layer in the atmosphere, animals and plants could not exist, at least upon land. It is therefore of the greatest importance to understand the processes that regulate the atmosphere's ozone content." (Royal Academy of Sciences, announcing the 1995 Nobel Prize for Chemistry for Paul Crutzen, Mario Molina, and F. Sherwood Rowland)

→The Ozone hole was initially detected in Antartida in 1985, by the team of Joseph Farman (English scientist).

→ Since then it has been constantly monitorated

1985: Vienna convention about the ozone hole problem.

Introduction

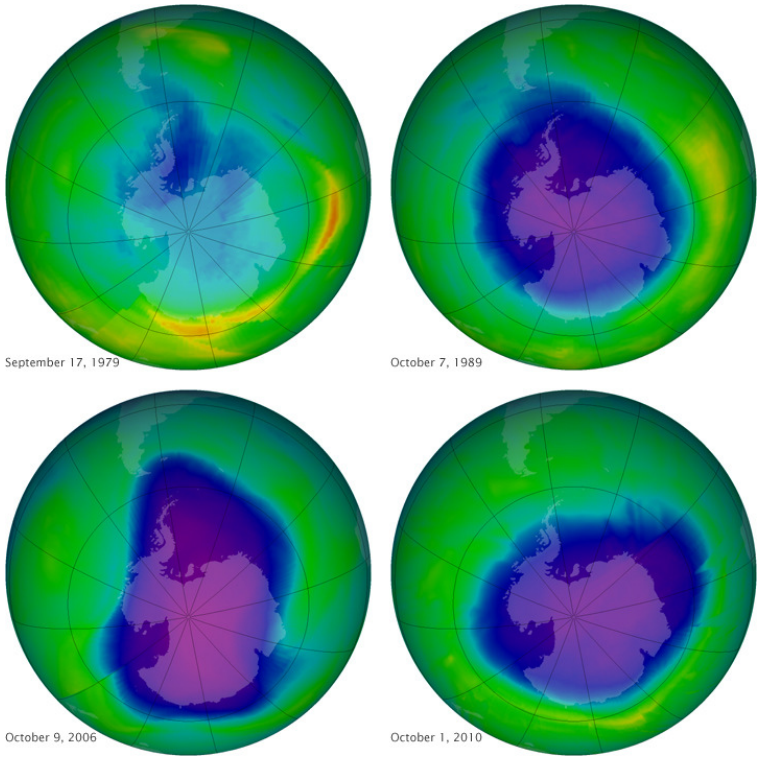
Ozone layer and the CFCs

1987: A team formed by 150 scientists from four countries went to Antartida and concluded that ClO concentration there was ~ **one hundred times larger than everywhere alse.**

1995: **Nobel prize to Rowland and Molina.**

Introduction

NASA monitoring

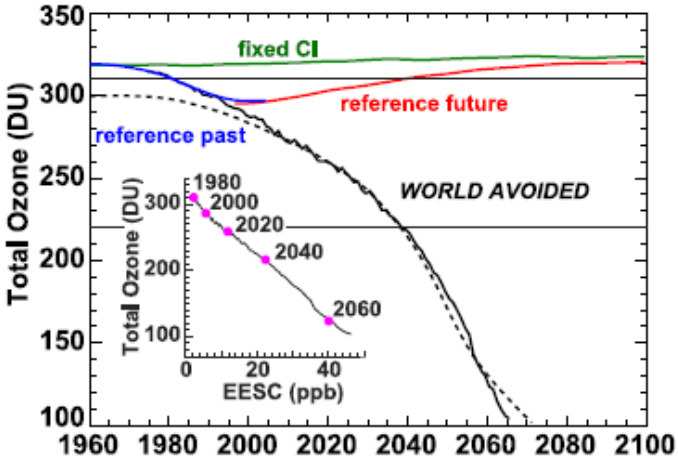


Introduction

NASA monitoring

What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?

→P. A. Newman et. al, *Atmos. Chem. Phys.*, 9, 2113, **2009**

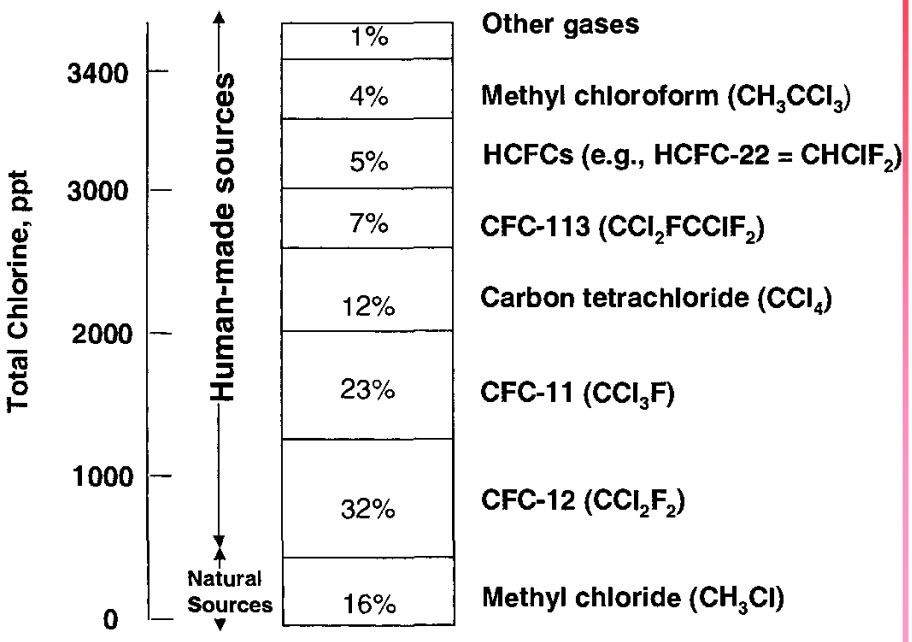


→Yes, scientific knowledge saved many lives !!

→ Other gases containing Cl (and Br) can also deplete the ozone layer!

→Main sources of Cl in the atmosphere(1999):

Source: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Second Edition, by John H. Seinfeld and Spyros N. Pandis. Copyright © 2006 John Wiley & Sons, Inc.



→ **ODP**: ozone depletion potential.

→Relative to CFC-11

Source: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Second Edition, by John H. Seinfeld and Spyros N. Pandis. Copyright © 2006 John Wiley & Sons, Inc.

TABLE 5.3 Steady-State Ozone Depletion Potentials (ODPs) Derived from Two-Dimensional Models[a]

Trace Gas	ODP
CFC-11 ($CFCl_3$)	1.0
CFC-12 (CF_2Cl_2)	0.82
CFC-113 ($CFCl_2CF_2Cl$)	0.90
CFC-114 (CF_2ClCF_2Cl)	0.85
CFC-115 (CF_2ClCF_3)	0.40
CCl_4	1.20
CH_3CCl_3	0.12
HCFC-22 (CF_2HCl)	0.034
HCFC-123 (CF_3CHCl_2)	0.012
HCFC-124 (CF_3CHFCl)	0.026
HCFC-141b (CH_3CFCl_2)	0.086
HCFC-142b (CH_3CF_2Cl)	0.043
HCFC-225ca ($CF_3CF_2CHCl_2$)	0.017
HCFC-225cb (CF_2ClCF_2CHFCl)	0.017
CH_3Br	0.37
H-1301 (CF_3Br)	12
H-1211 (CF_2ClBr)	5.1
H-1202 (CF_2Br_2)	1.3
H-2402 (CF_2BrCF_2Br)	<8.6
CH_3Cl	0.02

[a]World Meteorological Organization (2002).

→ HCFCs as substitutes

→As they have at least one H atom, they are consumed through reaction with •OH in the troposphere .

→Although they contain Cl, reaction with hidroxyl radical (•OH) decrease their probability to reach stratosphere.

→However, they contribute to the greenhouse effect…

→Their lifetimes are also important!

TABLE 2.15 Atmospheric Halogens

Compound	Generic Name	1998 Mixing Ratio (ppt)	Lifetime (yr)	Sources[a]	Sinks[b]
$CFCl_3$	CFC-11	268	45	A	Strat.$h\nu$
CF_2Cl_2	CFC-12	533	100	A	Strat.$h\nu$
$CF_2ClCFCl_2$	CFC-113	84	85	A	Strat.$h\nu$
CF_2ClCF_2Cl	CFC-114	15	300	A	Strat.$h\nu$
CCl_4	Carbon tetrachloride	102	35	A	Strat.$h\nu$
CH_3CCl_3	Methyl chloroform	69	4.8	A	Trop. OH
CH_3Cl	Methyl chloride	500	1.5	N(O),BB	Trop. OH
CF_2HCl	HCFC-22	132	11.9	A	Trop. OH
CH_3Br	Methyl bromide	9–10	0.8	N(O)A,BB	Trop. OH
CF_3Br	H-1301	2.5	65	A	Strat.$h\nu$
CF_4	Perfluoromethane	80	50,000	A	Meso.$h\nu$
SF_6	Sulfur hexafluoride	4.2	3200	A	Meso. electrons
CF_3CHCl_2	HCFC-123		1.4	A	Trop. OH
CF_3CHFCl	HCFC-124		5.9	A	Trop. OH
CH_3CFCl_2	HCFC-141b	10	9.3	A	Trop. OH
CH_3CF_2Cl	HCFC-142b	11	19	A	Trop. OH
$CF_3CF_2CHCl_2$	HCFC-225ca		2.5	A	Trop. OH
$CClF_2CF_2CHClF$	HCFC-225cb		6.6	A	Trop. OH
$CHCl_3$	Chloroform		0.55	A,N(O)	Trop. OH
CH_2Cl_2	Methylene chloride		0.41	A	Trop. OH
CF_3CF_2Cl	CFC-115	7	1700	A	Strat. $O(^1D)$
C_2Cl_4	Tetrachloroethene		0.4	A	Trop. OH

[a] A = anthropogenic; N(O) = natural (oceanic); BB = biomass burning.
[b] Strat. $h\nu$ = photolysis in stratosphere; Trop. OH = hydroxyl radical reaction in troposphere; Meso. electrons = mesosphere electron impact; Strat. $O(^1D)$ = reactions in stratosphere with excited atomic oxygen.
Sources: IPCC (2001) and Singh (1995).

Initial motivation to the study of Cl^- release

Works by the group of R. P. Tuckett

→ N.J. Rogers *et. al.*, PCCP, **2010**, 12, 10971

→**CH_3X** (X=F,Cl,Br); **Vacuum-UV negative photoion spectroscopy of CH_3F, CH_3Cl and CH_3Br**

$CH_3F \rightarrow F^- + CH_3^+$

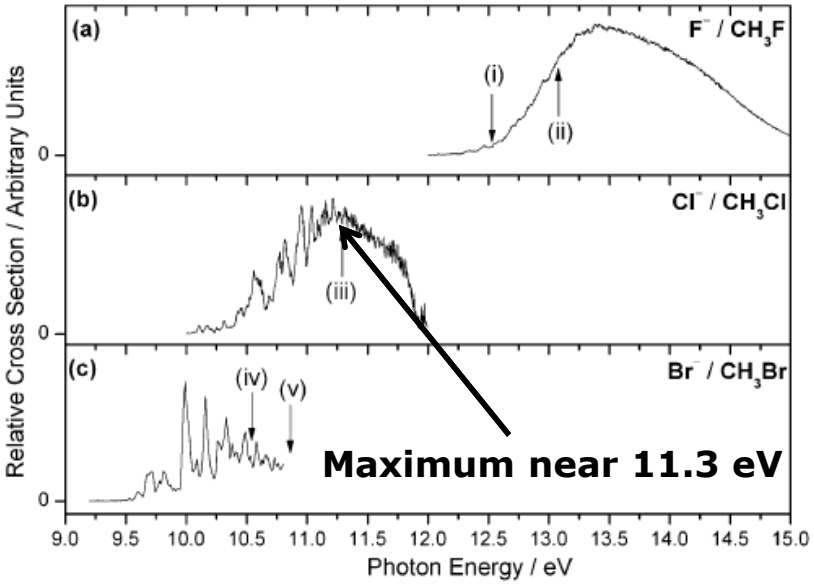
→**ΔH**= 11.18 eV

$CH_3Cl \rightarrow Cl^- + CH_3^+$

→**ΔH**= 9.85 eV

$CH_3Br \rightarrow Br^- + CH_3^+$

→**ΔH**= 9.53 eV



Resultados Experimentais

Rogers, et al. Phys. Chem. Chem. Phys. 2010(12) 10971–10980

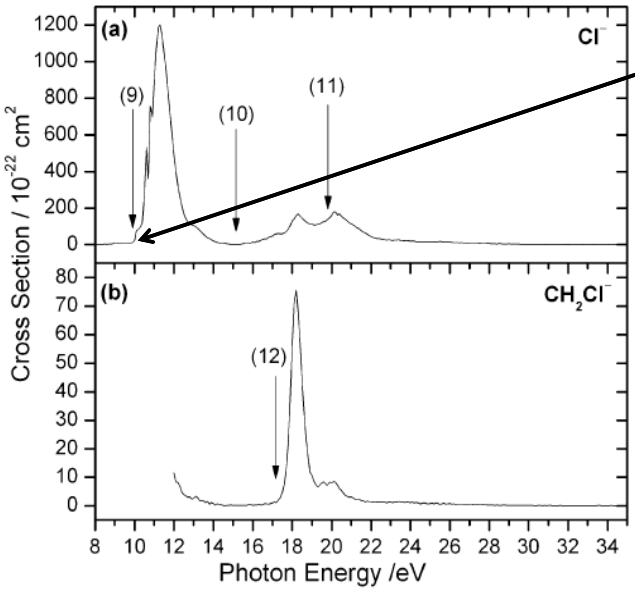


Fig. 2 Absolute cross sections for Cl^- (a) and CH_2Cl^- (b) production following vacuum-UV photoexcitation of CH_3Cl. Ion yields were measured between 8 and 34 eV at a wavelength resolution of 0.6 nm. Solid arrows show the energies of the thermochemical thresholds calculated for reactions (9)–(12) (Section 4.2).

$$CH_3Cl \rightarrow Cl^- + CH_3^+$$

$\rightarrow \Delta H = 9.85$ eV

The arrows in Fig. 2 show the calculated $\Delta_r H^o_{298}$ values for possible ion-pair dissociation reactions (9)–(12). They take values 9.85, 15.14, 19.85 and 17.19 eV, respectively.

$$CH_3Cl \rightarrow Cl^- + CH_3^+ \quad (9)$$

$$CH_3Cl \rightarrow Cl^- + CH_2^+ + H \quad (10)$$

$$CH_3Cl \rightarrow Cl^- + CH^+ + 2H \quad (11)$$

$$CH_3Cl \rightarrow CH_2Cl^- + H^+ \quad (12)$$

→Higher energy peaks can be associated to more fragments

Initial motivation to the study of Cl^- release

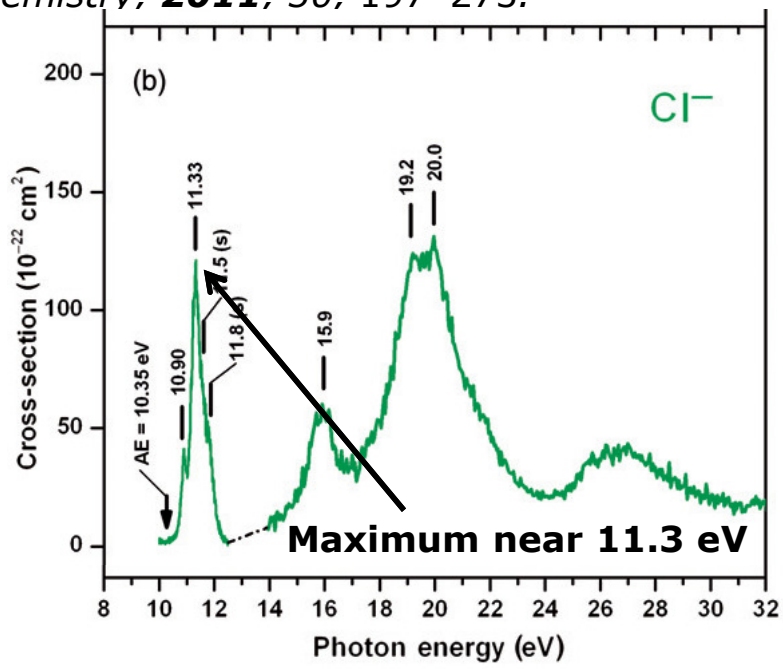
Works by the group of R. P. Tuckett

→ Vacuum-UV negative photoion spectroscopy of gas-phase polyatomic molecules,Simpson, M. J.; Tuckett, R. P. *International Reviews in Physical Chemistry*, ***2011***, *30*, 197–273.

→**CF_2Cl_2**

$$CF_2Cl_2 \rightarrow Cl^- + CF_2Cl^+$$

→**ΔH**= 8.2 eV



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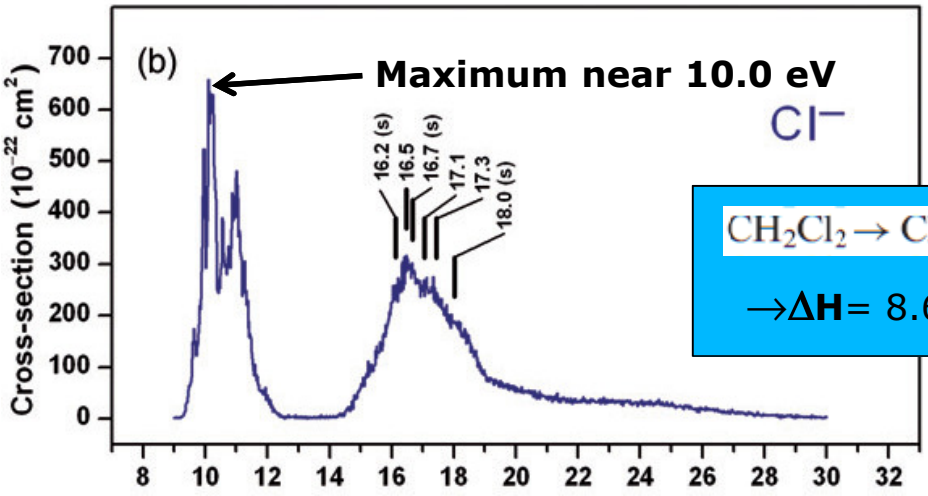
→ Vacuum-UV negative photoion spectroscopy of gas-phase polyatomic molecules,Simpson, M. J.; Tuckett, R. P. *International Reviews in Physical Chemistry, **2011**, 30,* 197–273.

→**CH_2Cl_2**



$CH_2Cl_2 \rightarrow Cl^- + CH_2\tilde{Cl}^+$

→**ΔH**= 8.6 eV

Initial motivation to the study of Cl^- release

Works by the group of R. P. Tuckett

→ Vacuum-UV negative photoion spectroscopy of gas-phase polyatomic molecules,Simpson, M. J.; Tuckett, R. P. *International Reviews in Physical Chemistry*, ***2011***, *30,* 197–273.

M.J. Simpson, R.P. Tuckett, K.F. Dunn, C.A. Hunniford, and C.J. Latimer, *Vacuum-UV negative photoion spectroscopy of CF_3Cl, CF_3Br and CF_3I*, *Journal of Chemical Physics* **130**, 194302,1–194302,11 (2009). *Reproduced

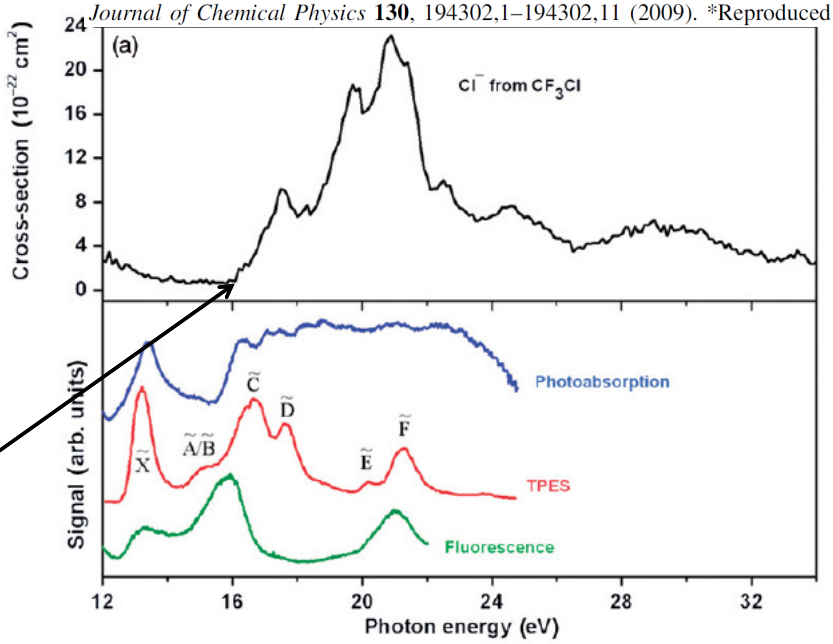
→**CF_3X** (X=Cl,Br,I);

$$CF_3Cl \rightarrow Cl^- + CF_3^+$$

→**ΔH**= 9.2 eV[4]

[4]M. J. Simpson, PhD Thesis, School of Chemistry, University of Birmingham, Aug. 2010

→ **Much higher onset! Why ??**



Mechanisms for ion-pair formation

M. J. Simpson and R. P. Tuckett, Int. Rev. Phys. Chem. 2011(30) 197–273

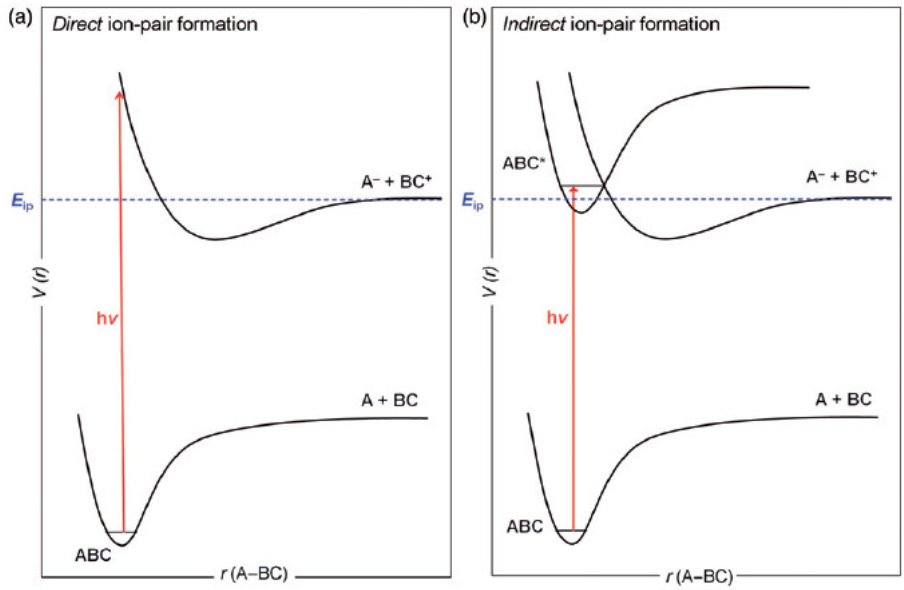


Figure 1 (colour online). (a) Potential energy (V) as a function of bond distance (r) showing *direct* ion-pair formation process for the generic reaction $ABC + h\nu \rightarrow A^- + BC^+$. E_{ip} represents the asymptotic ion-pair dissociation energy. (b) Potential energy (V) as a function of bond distance (r) showing *indirect* ion-pair formation process via predissociation of a neutral excited state (ABC*), i.e. $ABC + h\nu \rightarrow (ABC^*) \rightarrow A^- + BC^+$.

First outcome: nature of the bond in the ion-pair of CH_3Cl

RSC Advances 2014

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Cite this: *RSC Adv.*, 2014, 4, 64085

Valence and Rydberg states of CH_3Cl: a MR-CISD study

Vanessa C. de Medeiros, Silmar A. do Monte and Elizete Ventura*

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2016

Article

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Photochemistry of CH_3Cl: Dissociation and CH···Cl Hydrogen Bond Formation

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What is a Rydberg state ?

⇒ In molecules it was first suggest by N. Bohr

⇒ A molecular Rydberg state corresponds to an electronic state characterized by an excitation to a very diffuse orbital with $n > n_{valence}$

⇒ Consequently, this electron "sees" the molecule almost as a distant positive charge.

⇒ In many cases the excitation energy fits to the Rydberg formula:

$$\Delta E = \mathrm{IE} - Z/2(n - \delta_l)^2$$ (in Hartrees)

→(i) Rydberg series: 3s, 4s, 5s, ... ; 3p, 4p, 5p, ...; 3d, 4d, 5d ...

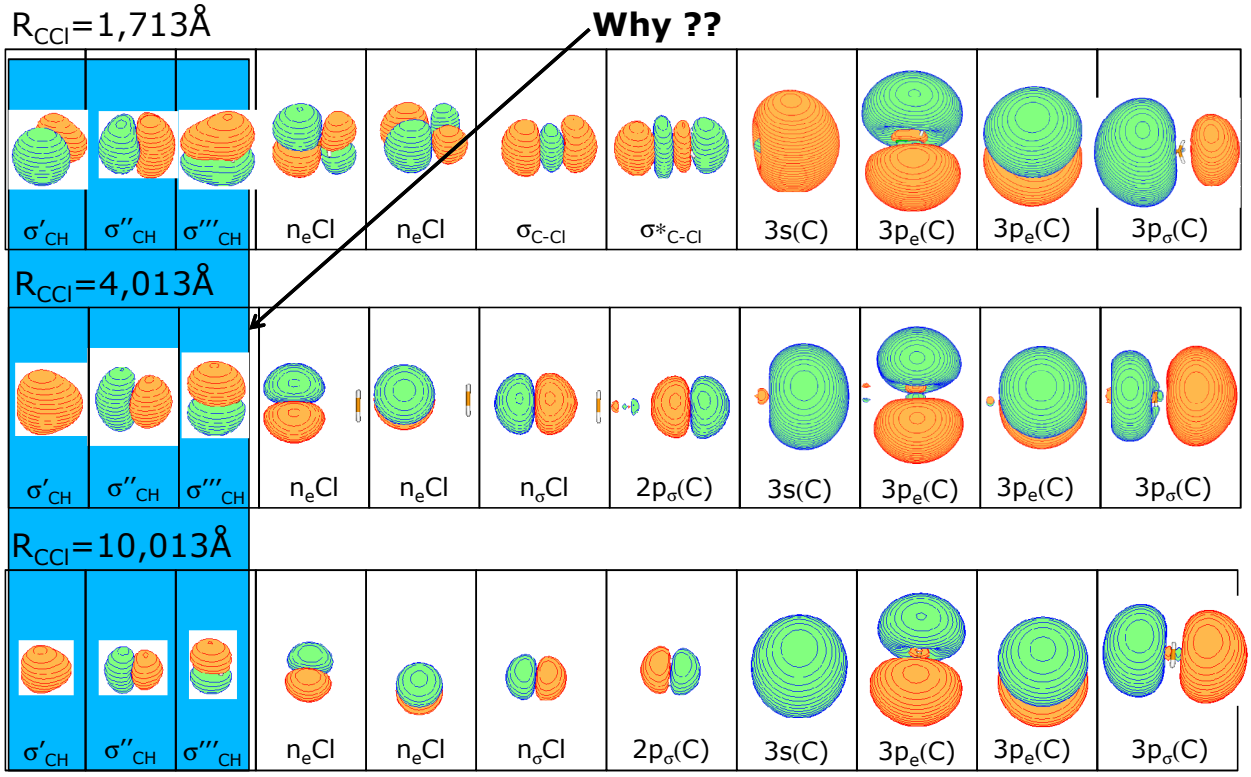
→(ii) Attempt to generalize the hydrogenic formula.

→(iii) δ_l : quantum defect: to take the electronic repulsion into account; atomic nature in a molecular orbital.

→(iv) IE : Ionization energy

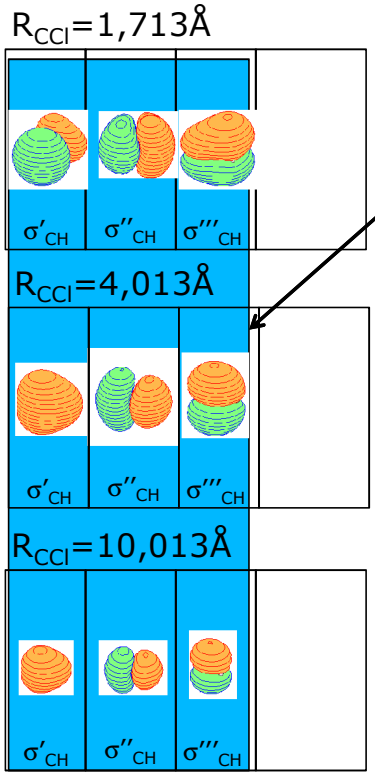
Results for CH_3Cl

Choice of active space



Results for CH_3Cl

Choice of active space



Why ??

→**(i)Mebel and Lin:** a valence state between two 3p states of CH_3[5]

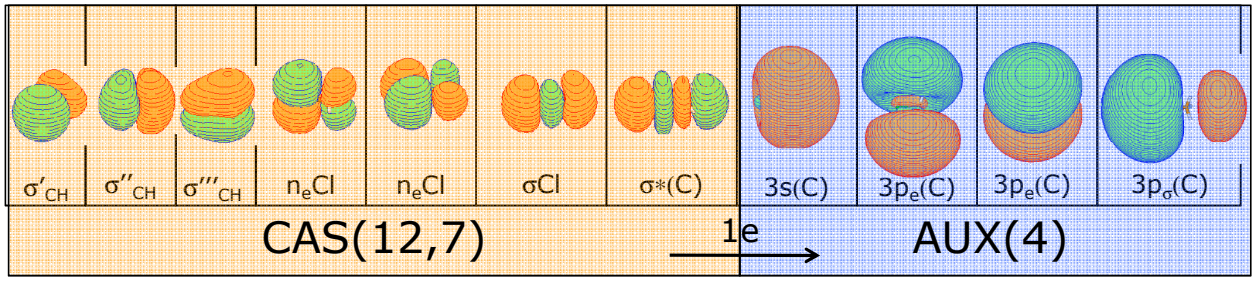
→**(ii)After many tests:** inclusion of these orbitals lead to correction dissociation (correct orbital shapes *and* degeneracies)

[5] Mebel, A. M.; Lin, S. *Chemical Physics* **1997,** *215,* 329–341.

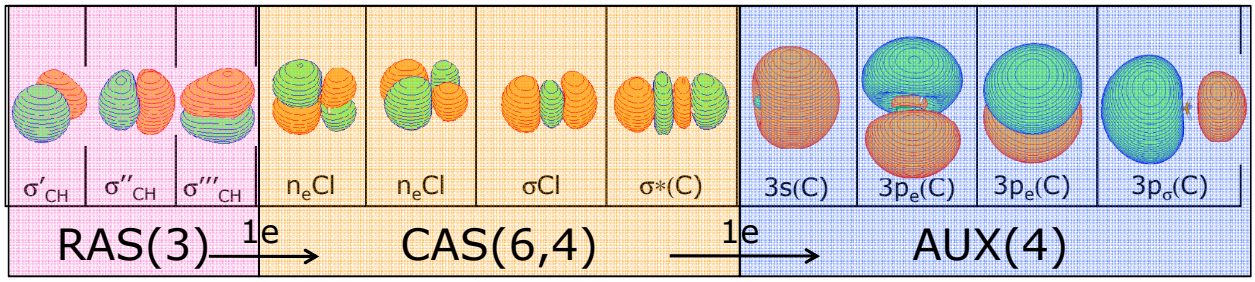
Results for CH_3Cl

Schemes used in the wavefunctions

scheme used at the MCSCF level

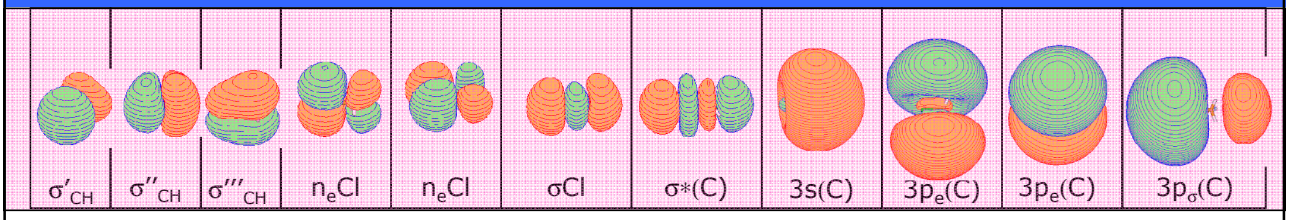


scheme used at the MR-CISD level



Results

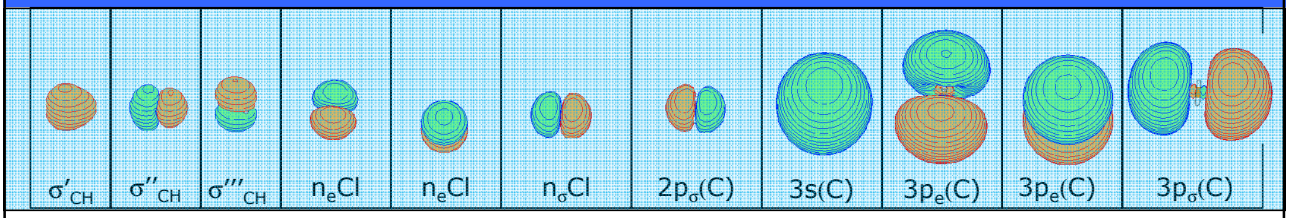
Eletronic states and configurations



	R_{CCl}=1,712Å
1^1A_1	(0.86)gs
1^1E	(0.54)$n_e\sigma^*$ + (0.24)n_e3s(C)
2^1E	(0.46)n_e3s(C) + (0.36)n_e3p_σ(C)
2^1A_1	(0.86)n_e3p_e(C)
3^1E	(0.88)n_e3p_e(C)
1^1A_2	(0.88)n_e3p_e(C)
4^1E	(0.44)n_e3p_σ(C)+(0.27)$n_e\sigma^*$+(0.17)n_e3s(C)
3^1A_1	(0.81)σ3s(C)
4^1A_1	**(0.71)σ$3p_\sigma$(C)+ (0.15)σσ***
5^1E	(0.86)σ$3p_e$(C)
5^1A_1	(0.73)$\sigma_{CH}\sigma^*$

Results

Eletronic states and configurations



	R_{CCl}=1,712Å
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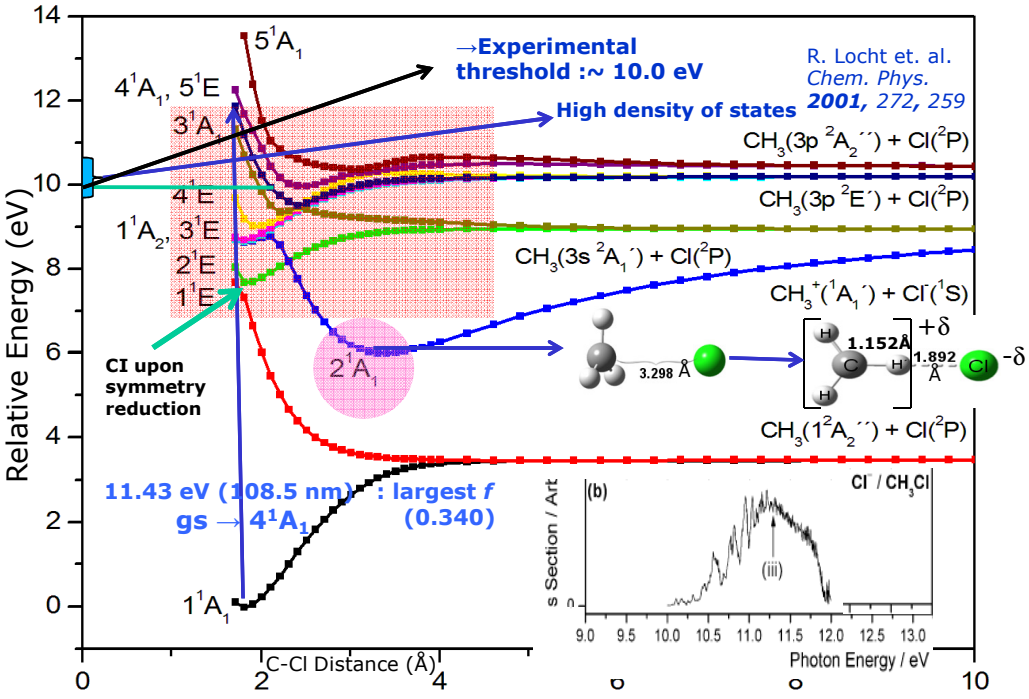
4^1E	(0.44)n_e3p_σ(C)+(0.27)$n_e\sigma^*$+(0.17)n_e3s(C)
3^1A_1	(0.81)σ3s(C)
4^1A_1	(0.71)σ$3p_\sigma$(C)+ (0.15)σσ*
5^1E	(0.86)σ$3p_e$(C)
5^1A_1	(0.73)$\sigma_{CH}\sigma^*$

	R_{CCl}=10,013Å
$1^1A_1+1^1E$	$(2p_\sigma)^1n(Cl)^5$
2^1A_1	$(2p_\sigma)^0n(Cl)^6$ (ionic)
$2^1E+3^1A_1$	$(n_\sigma,n_\varepsilon)^4$ 3s(C)^1
$3^1E+4^1E+1^1A_2+4^1A_1$	$(n_\sigma,n_\varepsilon)^4$ $3p_\varepsilon$(C)^1
$5^1A_1+5^1E$	$(n_\sigma,n_\varepsilon)^4$ $3p_\sigma$(C)^1

Results

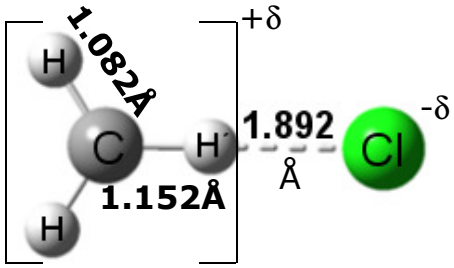
Potential energy curves

Curves at MR-CISD/aug-cc-pVDZ(Cl,H)/d-aug-cc-pVDZ (C) level



Results

Some characteristics of the hydrogen bonded contact ion-pair



(i) Charge separation: δ = 0,88;

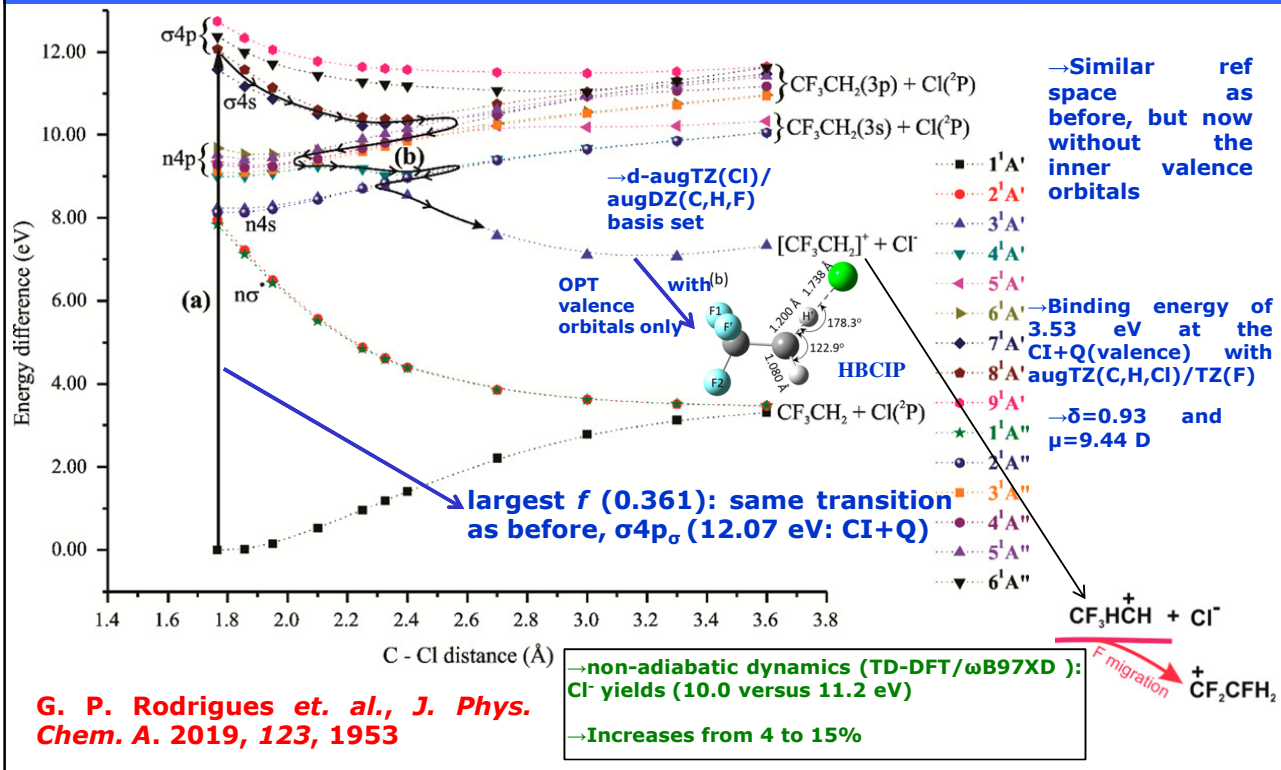
(ii) Highly polar: 10,41 D (MR-CISD with augTZ(H,Cl)/d-aug-TZ(C) basis set);

(iii) Configuration: $0{,}75(2p_{\sigma}(C))^{0}(n_{\sigma}(Cl))^{2} + 0{,}11\sigma\sigma^{*}$

(iv) Binding energy: 4.65 eV (MR-CISD+Q/valence with ZPE and augTZ(H,Cl)/d-aug-TZ(C) basis set)

Results

Continuation ... HCFC-133a (CF_3-CH_2Cl)



→Similar ref space as before, but now without the inner valence orbitals

→Binding energy of 3.53 eV at the CI+Q(valence) with augTZ(C,H,Cl)/TZ(F)

→δ=0.93 and μ=9.44 D

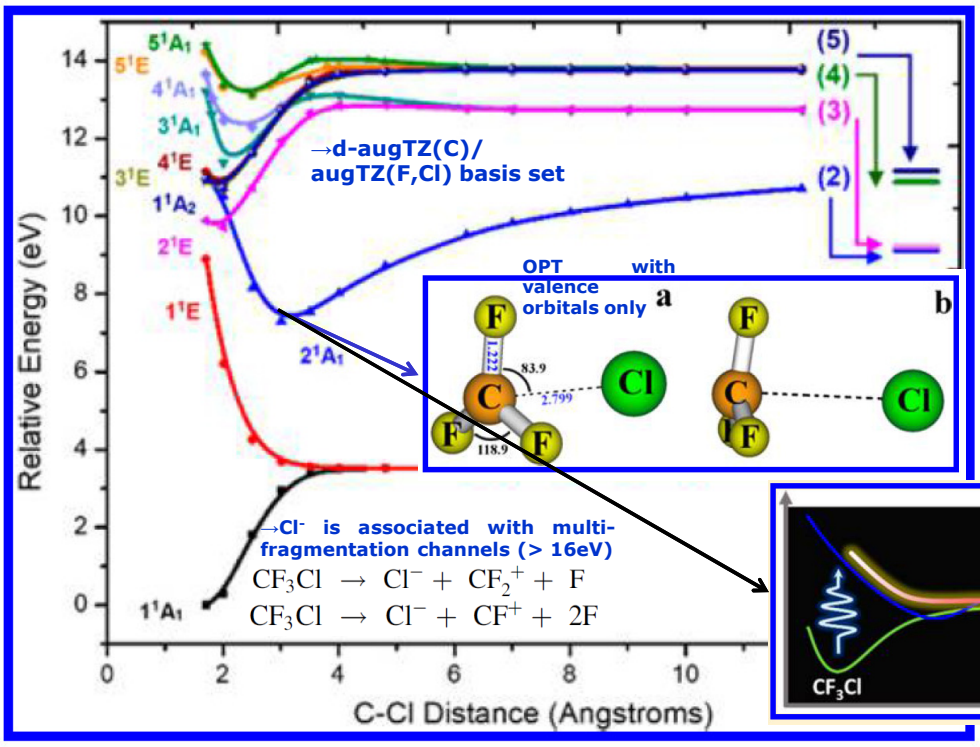
→non-adiabatic dynamics (TD-DFT/ωB97XD): Cl^- yields (10.0 versus 11.2 eV)

→Increases from 4 to 15%

G. P. Rodrigues *et. al., J. Phys. Chem. A*. 2019, *123*, 1953

Results

CF_3Cl: sometimes the ion-pair is very close to a nearby state



→Similar ref space as that of CH_3Cl (RAS, CAS, AUX), but now the inner valence (RAS) is a n_F orbital

→Binding energy of 4.0 eV

→δ=1.42 and μ = 11.56 D

V. C. de Medeiros *et. al.*, JCTC (2018), 14, 4844

Under study

Hydrogen bonded contact ion-par in CH_3-CH_2Cl

J. Phys. Chem. A, Vol. 101, No. 7, 1997

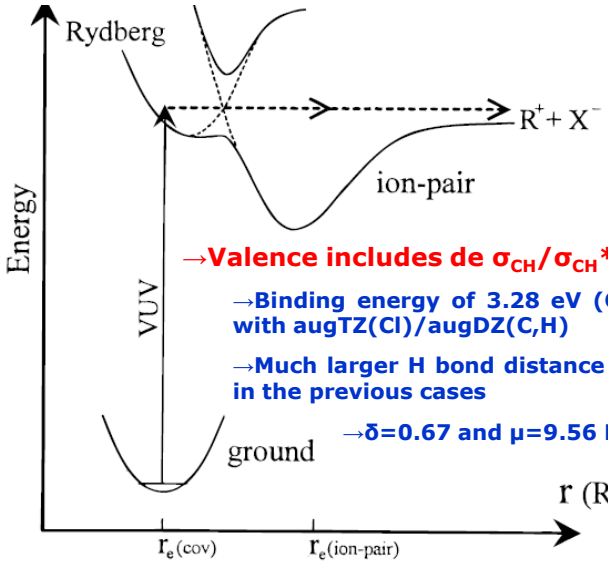


Figure 1. Photopreparation of a Rydberg state and dissociation of a ion-pair state of alkyl halides by vacuum ultraviolet excitation.

→Valence includes de σ_{CH}/σ_{CH}* pair

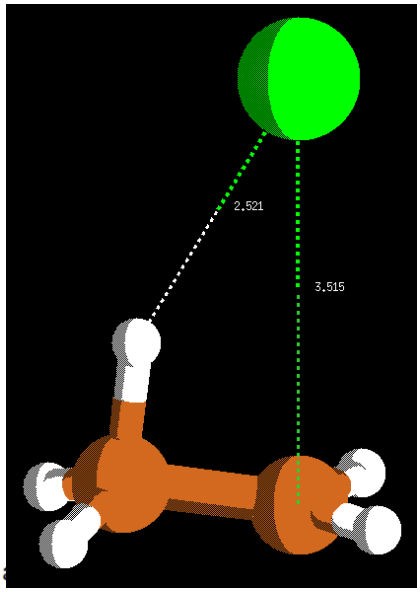
→Binding energy of 3.28 eV (CI+Q with augTZ(Cl)/augDZ(C,H)

→Much larger H bond distance than in the previous cases

→δ=0.67 and μ=9.56 D

→Phodissociation at 10.48 eV

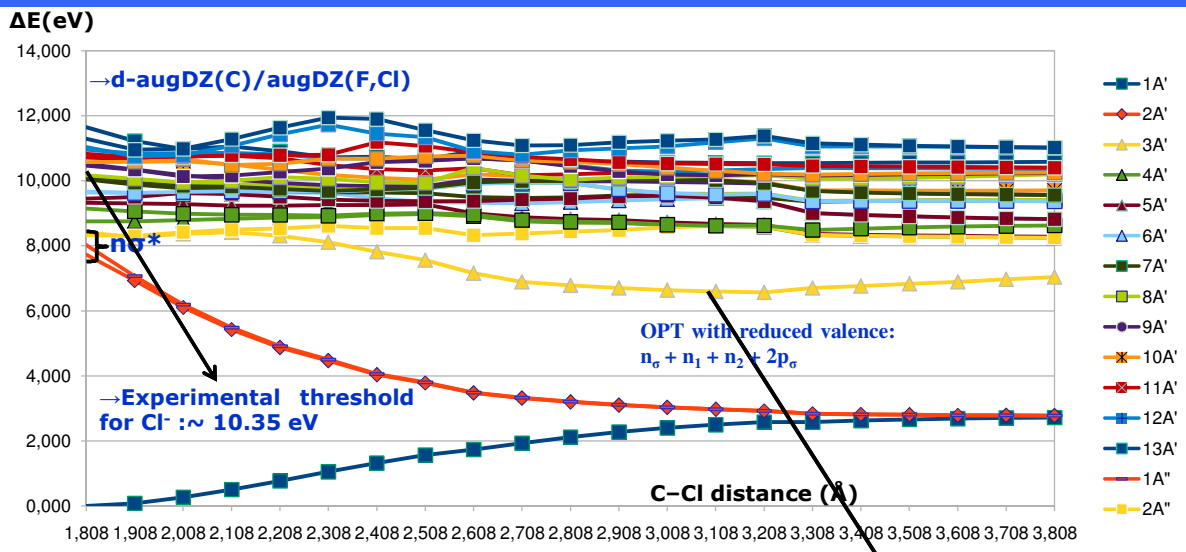
→Focused on the R^+ fragment



→Hydrogen shared and 3 orbitals in the ethyl cation

Under study

CF_2Cl_2 , MCSCF: 2σ pairs + 4n(Cl) + AUX(3s(C), 3p(C)) (also CH_2Cl_2)



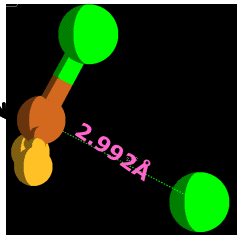
→The four lowest excited states are nσ*, at both MCSCF and CI levels

→There are nσ* states of much higher energies

→Structure similar to that of $[CF_3]^+Cl^-$ but ~ 0.193Å longer

→ δ = 0.60, μ = 7.51D and binding energy of 3.00 eV at CI +Q(complete valence)/augDZ

→ Next lower state 0.32 eV lower (at CI level): deactivation ?



Conclusions

→High level MR-CISD calculations are required for details concerning photochemical reactions (dissociation channels, emitting structures (fluorescence), minima, conical intersection (deactivation), ...)

→A judicious choice of orbitals is crucial ! Sometimes a RAS/CAS/AUX scheme is necessary

→Computational effort versus accuracy

→For the studied chloroalkanes the generated Cl (or Cl^-) atom is in its ground state: at the end the excitation energy is in the fragment (methyl, ethyl, CF_3, CF_3CH_2, ...)

→The $C^+-H\cdots Cl^-$ moiety (observed in the CH_3Cl and CF_3CH_2Cl systems) is an uncommon structure, but here it has been observed in excited states

→It has been observed previously (though in the ground state) in systems where the C atom is part of a heteroaromatic ring (in ionic liquids)

→Deactivation of the ion-pair can take place