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Electronic structure and thermodynamic and kinetic properties of radical cations of alkenes

Estructura electrónica y propiedades termodinámicas y cinéticas de radicales catiónicos derivados de alquenos

Estrutura electrónica e propiedades termodinámicas e cinéticas de radicaís catiónicos derivados de alquenos

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Abstract

Alkenes and enol ethers are structures that are frequently found in many biomolecules. When sunlight interacts with them, a photoionization reaction can take place, producing radical cations, which can be harmful for living organisms.

In this piece of research electronic properties of ethylene, tetramethylethylene, tetramethoxyethylene and their corresponding radical cations were measured in vacuum and in aqueous solution with computational chemistry models. DFT method with 6-311G as basis set was used to develop the electronic calculations and SMD model was used to simulate water as solvent. Electronic structure calculation software Gaussian and the supercomputer at the supercomputing Galician centre (CESGA) were used to carry out all the calculations.

Calculations developed to study the mentioned molecules were: molecular structure optimization from an optimization + frequency calculation, NBO analysis, UV-Vis spectrum and IR + Raman spectrum. Obtained results suggest that radical cation is less stable than the neutral species, and so, more reactive than that, and aqueous solution is able to stabilize it. Ethylene radical cation is the most destabilized followed by TME, in which methyl substituents act as electron donating groups, TMOE is the most stabilized radical cation as oxygen is able to donate a high amount of electronic density to the central carbon atoms of the molecule. A change in the molecule and molecular orbitals symmetry is obtained when shifting from the neutral species to the radical cation. Furthermore, reduction potentials are calculated with the direct method, ionization potentials are estimated with Koopmans' theorem and spectra analysis is developed.

Key words: photoionization, radical cation, alkene, enol ether, computational chemistry, DNA damage, Gaussian.

Resumen

Los alquenos y enol éteres son estructuras que se encuentran con frecuencia en muchas biomoléculas. Cuando la luz solar interactúa con ellos, se puede promover una reacción de fotoionización que conduce a la formación de un radical catión, que puede ser perjudicial para el organismo.

En esta investigación se midieron las propiedades electrónicas del etileno, tetrametiletileno, tetrametoxietileno y sus correspondientes radicales cationes en vacío y en disolución acuosa con modelos de química computacional. Se utilizó el método DFT con 6-311G como conjunto base para desarrollar los cálculos electrónicos y el modelo SMD se utilizó para simular el agua como disolvente. Para realizar todos los cálculos se utilizó el software de cálculo de estructuras electrónicas Gaussian y el superordenador del centro gallego de supercomputación (CESGA).

Los cálculos que se usaron para estudiar las moléculas mencionadas fueron: optimización de la estructura molecular a partir de un cálculo de optimización + frecuencia, análisis NBO, espectro UV-Vis y espectro IR + Raman. Los resultados obtenidos sugieren que el radical catión es menos estable que la especie neutra, y, por lo tanto, más reactivo que esta, y el medio acuoso es capaz de estabilizarlo. El radical catión del etileno es el más desestabilizado seguido por el del TME, en el que los sustituyentes metilo actúan como grupos donantes de electrones, TMOE es el radical catión más estabilizado ya que el oxígeno es capaz de donar una alta cantidad de densidad electrónica a los átomos de carbono centrales de la molécula. Se obtiene un cambio en la simetría de la molécula y en los orbitales moleculares al pasar de la especie neutra al radical catión. Además, los potenciales de reducción se calculan con el método directo, los potenciales de ionización se estiman con el teorema de Koopman y se desarrolla el análisis de los espectros.

Resumo

Os alquenos e os enol éteres son estruturas que se atopan con frecuencia en moitas biomoléculas. Cando a luz solar interactúa con eles, pódese promover una reacción de fotoionización que conduce á formación dun radical catión, que pode ser prexudicial para o organismo.

Nesta investigación medíronse as propiedades electrónicas do etileno, tetrametiletileno, tetrametoxietileno e os seus correspondentes radicais catións en baleiro e en disolución acuosa con modelos de química computacional. Fíxose uso do método DFT con 6-311G como conxunto base para desenvolver os cálculos electrónicos e fíxose uso do modelo SMD para simular o auga como disolvente. Para realizar todos os cálculos utilizouse o software de cálculo de estruturas electrónicas Gaussian e o superordenador do centro galego de supercomputación (CESGA).

Os cálculos que se usaron para estudar as moléculas mencionadas foron: optimización da estrutura molecular a partir dun cálculo de optimización + frecuencia, análise NBO, espectro UV-Vis e espectro IR + Raman. Os resultados obtidos suxiren que o radical catión é menos estable que a especie neutra, e, polo tanto, é máis reactivo que esta, ademais o medio acuoso é capaz de estabilizalo. O radical catión do etileno é o máis desestabilizado seguido polo do TME, no que os substituíntes metilo actúan como grupos donantes de electróns, TMOE é o radical catión máis estabilizado xa que o osíxeno é capaz de doar unha alta cantidade de densidade electrónica aos átomos de carbono centrais da molécula. Obtense un cambio na simetría da molécula e nos orbitais moleculares ao pasar da especie neutra ao radical catión. Ademais, os potenciais de redución calcúlanse co método directo, os potenciais de ionización estímense co teorema de Koopman e desenvólvese o análise dos espectros.

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Abbreviations

CC	Computational Chemistry
CESGA	Centro de Supercomputación de Galicia (Galicia Supercomputational Centre)
DFT	Density Functional Theory
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
IE	Ionization Energy
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
N	Neutral
NBO	Natural Bond Orbital
NHE	Normal Hydrogen Electrode
ON	Orbital Number
OT	Orbital Type
RC	Radical Cation
ROS	Reactive Oxygen Species
SCRf	Self-Consistent Reaction Field
SMD	Solvation Model Based on Density
TD-DFT	Time-Dependent Density Functional

TME

TMOE

UV-Vis

Theory

Tetramethylethylene

Tetramethoxyethylene

Ultraviolet-Visible

Introduction

Sunlight is necessary for life and it has always been considered as a source of health. Nevertheless, despite its benefits, a prolonged exposition to solar radiation can cause harmful effects in living organisms, such as skin burns, cell damage and death, DNA alterations, skin cancer, etc.¹

A type of reactions that are promoted by sunlight and which can cause damage to organisms are photoionization reactions. Photoionization reactions take place when the interaction of a photon with an atom or molecule leads to the formation of its cation. When this process occurs in a close-shell molecule the ionic species formed has an unpaired electron and it's called radical cation.

This project focused on studying electronic properties of alkenes and enol ethers, whose structure is present in many biomolecules, and their corresponding radical cations, which can be generated as a consequence of the action of the most energetic fraction of sunlight (UV-B) on the skin and eye mucous. Molecules studied were ethylene, tetramethylethylene and tetramethoxyethylene, whose structure is shown in figure 1.

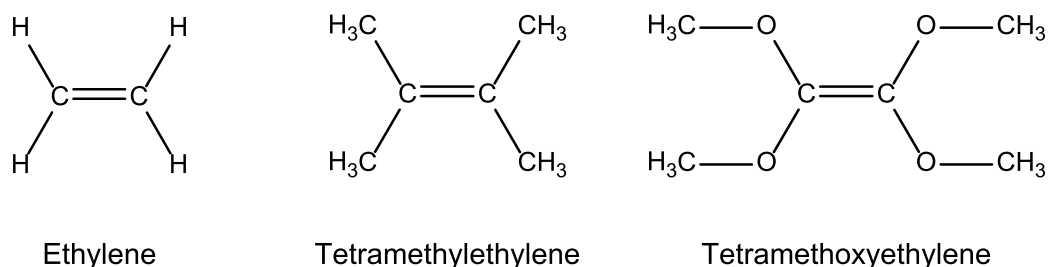


Figure 1. Structure of studied molecules

Geometric and electronic parameters, an NBO analysis and IR, Raman and UV-Vis spectra from those species were calculated with the computational chemistry method of the Density Functional Theory (DFT). An analysis in aqueous solution was also simulated with the solvation model based on density (SMD). Moreover, redox potentials for the radical cations were estimated with the direct method.

Electronic structure calculations based on quantum mechanics were performed using the electronic structure calculation software Gaussian and the supercomputer at the supercomputing Galician centre (CESGA).

Objectives

The aim of this research is to study the structure, bonding, electronic properties and stability of ethylene, tetramethylethylene, tetramethoxyethylene and their corresponding radical cations in order to understand better their reactivity. The specific objectives are:

1. Learning to use the Finis Terrae III supercomputer (CESGA).
2. Handling of computer modelling programs (Gaussian16, Gaussian09, GaussView, Mercury, ChemDraw).
3. Learn the basis of Computational Chemistry.
4. Molecular structure optimization of ethylene, tetramethylethylene, tetramethoxyethylene and their corresponding radical cations in vacuum and in aqueous solution.
5. NBO analysis of the studied species.
6. Calculation of the UV-Vis, Raman and IR spectra of the studied molecules.
7. Critical analysis of the results and relate them with concepts learned along the Chemistry degree.

Timeline

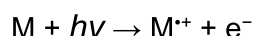
Activities developed throughout the current Bachelor final degree dissertation chronologically ordered are shown next:

February	March	April	May	June	July
Connection to CESGA					
Use of computer modelling programs					
	Bibliographic search			Bibliographic search	
Optimization of molecular structure					
				NBO analysis	
				Calculation of UV-Vis spectra	
				Calculation of Raman, IR spectra	
				Calculation of studied variables	
					Analysis of the results
	Memory writing			Memory writing	

Background

Generation of radical cations by photoionization

If a photon collides with an atom or molecule, and the energy of the photon is absorbed by them, the corpuscle will be promoted to an excited state. In a photoionization process an electron is provided with enough energy to break away the binding forces of the atom or molecule and ionize it, as it's shown in the reaction:



The minimum energy required to remove an electron from an isolated atom or molecule is called the ionization energy (or ionization potential). In a molecule, the ionization potential can be either vertical or adiabatic. The geometry of an ion may differ from the neutral species, the vertical ionization energy is the energy associated with the transition from the molecule in its ground vibrational state to the cation in an excited vibrational level whose wavefunction has the highest overlap with that of the molecule in its ground state, i.e. the ion has a geometry similar to the neutral species. On the other hand, the adiabatic ionization energy is the energy associated with the transition from the molecule in its ground vibrational state to the cation in its lowest vibrational energy level, i.e. in its relaxed geometry. In figure 1, vertical and adiabatic ionization energies are represented.^{2,3}

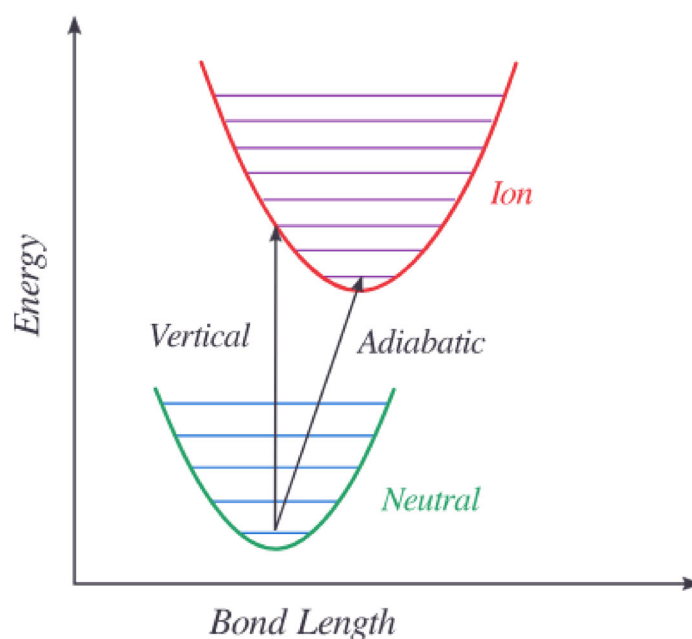


Figure 1. Representation of the vertical and adiabatic ionization potentials.³

The transition involved in the vertical ionization energy is the most probable one and it's related with the molecular orbital energy by the Koopmans' theorem, which states that the first ionization energy of a molecule is equal to the negative of the energy of the highest occupied molecular orbital (HOMO).^{2,4}

In a photoionization reaction part of the energy provided by the incoming photon is employed in ionizing the species and the excess energy is partitioned between the cation and the electron kinetic energy, so that the energy is conserved and the resonance condition, fulfilled.

$$h\nu = IE_i + T_{ion} + T_e$$

Where IE_i is the ionization energy of an electron in orbital i , T_{ion} is the cation kinetic energy and T_e is the electron kinetic energy. Because the mass of the atomic nucleus is much larger than the mass of the electron, the kinetic energy of the cation can be considered negligible.⁵

When this process takes place in a close-shell molecule with net charge equal to zero, the cationic species that is formed has an unpaired electron. It is, therefore, an open-shell species, paramagnetic, which is called radical cation.

Not all photon-molecule interactions result in photoionization. The probability of photoionization taking place, in fact, is related to the cross section of the molecule, which is related to the energy of the photon and the molecule itself. The cross-section can be estimated from the Franck-Condon factors between a molecule in its ground-state and the ion expected to be formed. For photon energies below the ionization threshold, the cross-section approaches to zero. In lasers, and specially in pulsed lasers, multi-photon processes may take place and the probability of photoionization increases by consecutive excitation processes and addition of the respective cross sections.

Differences between the properties and reactivity of closed shell species and radicals

"The same thing that makes you live can kill you in the end."

Neil Young

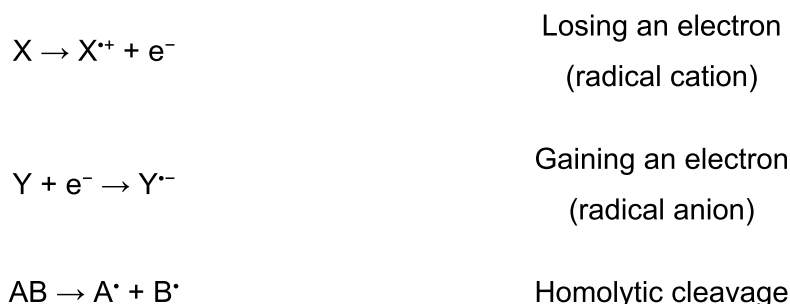
It's well known that oxygen is required for almost all the living organisms because it's

involved in the production of energy for the cell functioning but, actually, O₂ is a toxic and mutagenic gas. In 1954 Rebecca Gershman and Daniel L. Gilbert proposed that oxygen free radicals are the responsible for its toxicity.^{6,7}

Radicals are chemical fragments that contain at least an unpaired electron. Such situation is usually rather unstable so they tend to react to capture another electron to become a closed-shell species. That is the basis for their reactivity, which is usually very high although some exceptions can be found in species stabilized by resonance or by inductive effects.⁷

Radicals may have very different thermodynamic and kinetic behaviour, usually they are highly unstable but show a low reactivity towards closed-shell species, as the reaction between species with different multiplicities is forbidden by the spin conservation selection rule ($\Delta S=0$).

Radicals can be formed by losing an electron, by gaining one or by breaking a covalent bond by homolytic cleavage. The energy required to promote those reactions can be provided by heat, UV light and ionizing radiation.⁶



In biology, oxygen radicals are of great interest because they are intermediates in biological processes, two important ones are the hydroxyl radical (HO[•]) and the superoxide radical anion (O₂^{•-}). These are part of a group of compounds called reactive oxygen species (ROS), which includes radicals with an unpaired electron on oxygen, which means that the probability density of finding the unpaired electron close to the oxygen is higher than in any other part of the molecule (where HO[•] and O₂^{•-} are included), and products containing molecular oxygen, like H₂O₂.⁷

Origin of the photooxidative damage to biomolecules

The concept of oxidative stress needs to be introduced prior to talking about photooxidative damage: in aerobic organisms, reactive species are produced by endogenous and exogenous sources and their levels are controlled by antioxidant

defence systems. When the amount of reactive species (oxidants) is too high for the antioxidants available, that's called a state of oxidative stress.⁷ If oxidants exposure is low, oxidant signalling will address specific targets (oxidative eustress) and, on the other hand, if the exposure is high, redox signalling gets disrupted and biomolecules get damaged (oxidative distress).⁸

The skin and the eye are parts of human body that are exposed to light, which can promote several chemical and biological reactions. When a photosensitizer is excited electronically by light, it can react to form radical intermediates in different ways. In Type I reactions, radicals are formed through electron or hydrogen transfer, ROS are included there. In Type II reactions, the energy of the excited photosensitizer is employed to generate singlet molecular oxygen ($^1\text{O}_2$), which may react to form peroxides that can either decompose to radicals or react with other biomolecules producing lipid peroxidation. UVB light has enough energy to induce the homolytic cleavage of hydrogen peroxide and lipid hydroperoxides, producing radical intermediates, which damage biomolecules.⁸

DNA damage

The main cause of biologic effects from radiation is the cellular DNA damage, which can be of 2 types: direct and indirect. The first one consists in the absorption of a photon by an atom which releases an electron that interacts directly with DNA. While the second one occurs when the released electron reacts first with other molecules in cells, particularly with water, and DNA damage is caused by the free radicals produced, such as hydrogen atoms (H), hydroxy radicals ($\text{HO}\cdot$) and superoxide radical anions ($\text{O}_2^{\bullet-}$).

DNA damage produced by radiation can lead to either single-strand or double-strand breaks, of which the second type is considered as a cause of cell-death due to the complexity of the repairing mechanisms that need to take place in a cell to restore the original DNA coding sequence. Single-strand break may lead to a correct repair or lead to mutation.⁹

Molecules studied

In this research alkenes and enol ethers, which are present in many biomolecules, as well as their corresponding radical cations were studied. Ethylene was selected because it's the simplest alkene, tetramethylethylene and tetramethoxyethylene were selected in order to study different substituents and see how they affect to the reactivity and stability

of the molecule. In this sequence, electron donating groups are added to the double bond to stabilize the one-electron deficiency generated during photoionization and in the radical cation.

It was already said that solar radiation can induce photoionization. Figure 2 shows the reaction expected when UV photons induce photoejection of an electron from the tetramethylethylene molecule. After the radical cation is generated in aqueous media, water reacts very fast with it to yield an HO-adduct (figure 3).

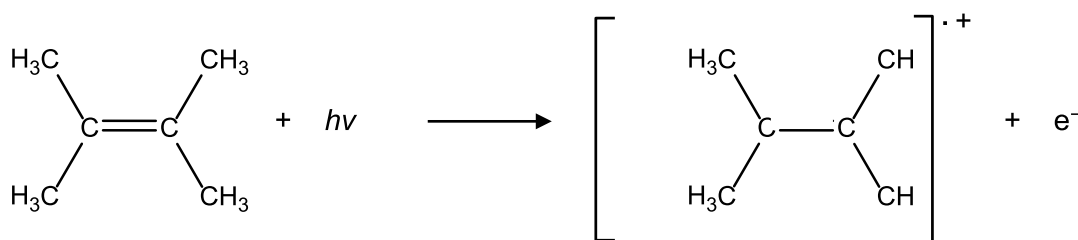


Figure 2. Generation of the radical cation of tetramethylethylene promoted by light.

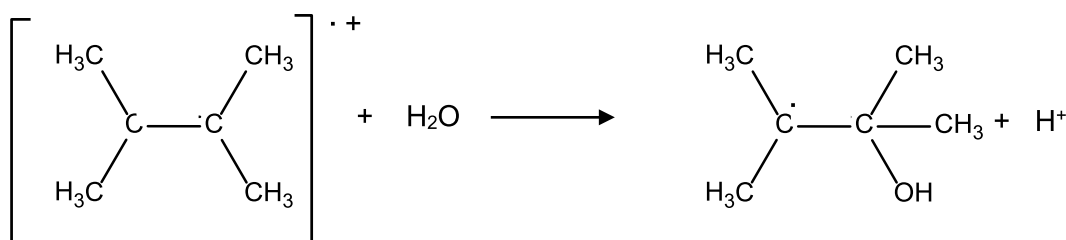


Figure 3. Reaction of water with the radical cation.

It can be observed how in the radical cation both the positive charge and the unpaired electron are delocalized and, after the reaction with water, the positive charge is localized on the H atom and the radical on the C vicinal to the OH. In the radical cation, the positive charge and the radical are stabilized by resonance and by inductive effects, while in the hydrated species the radical is only stabilized by inductive effects.

Alkenes

Molecular orbital (MO) theory extends the concept of an atomic orbital to a molecular orbital, a wavefunction that encompasses all the atoms in a molecule. In this section, MO theory will be applied to the simplest alkene, ethylene, in order to understand the

chemical bond in alkenes. Ethylene orbital configuration contains four 1s orbitals from the four H atoms and two 2s, 2p_x, 2p_y and 2p_z orbitals from the two C atoms. 1s, 2s, 2p_x and 2p_y orbitals contribute to the formation of the σ framework of the molecule, while 2p_z orbitals, which are perpendicular to the C-C σ bond, contribute to the formation of MOs of π character. In figure 4, MOs of ethylene resulting from the overlap of MOs from two fragments CH₂ is represented. MOs which are symmetric with respect to reflexion through a mirror plane containing the bond axis are designated as bonding σ and antibonding σ* orbitals and orbitals that are antisymmetric through this plane are called π and π* orbitals.¹⁰

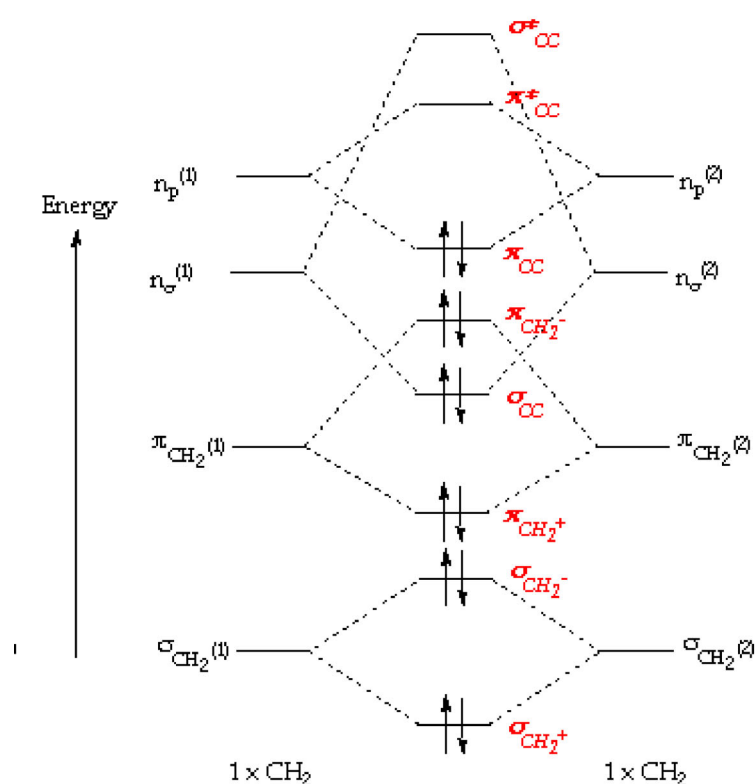


Figure 4. Representation of ethylene MOs.¹¹

The π bond in ethylene is weak compared to the C-C σ bond, what makes the π bond, and, thus, the overall molecule, highly chemically reactive.¹² Another consequence of the weakness of the π bond is that the energy stabilization in the bonding π orbital and the destabilization in the corresponding anti-bonding orbital π* are smaller than in σ orbitals,

that's the reason why usually the MOs with π character correspond to the HOMO and the LUMO.¹⁰

Enol ethers

Alkoxy substituents raise a lot the reactivity of C-C double bonds by increasing their nucleophilicity. This can be explained in terms of resonance stabilization of the positive charge in the enol ether carbocation (18).¹³ See figure 5.

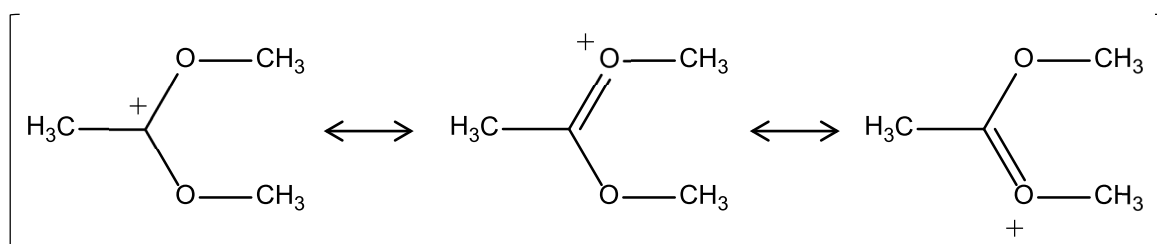


Figure 5. Stabilization by resonance of the positive charge in 1,1-dimethoxyethene.¹³

But further substitution than 1,1-dimethoxyethene, as occurs in tetramethoxyethene, will lead to a decrease in reactivity. On the one hand, because the additional substituents will not contribute to the stabilization of the positive charge by resonance and, on the other hand, because of the fact that alkoxy substituents are able to stabilize C-C double bonds, what will decrease the energy of the initial state of the reaction, raising, in that way, the reaction barrier and, thus, decreasing the reaction rate.¹³

Methods

Hardware

Electronic structure calculations were performed in Finis Terrae III, a supercomputer situated in the Galician supercomputing centre, CESGA (Centro de Supercomputación de Galicia).

Software

Gaussian09 was used to carry out all the calculations. This is a computational chemistry software package which performs electronic structure calculations to calculate molecular properties by using quantum mechanical descriptions for wave functions and electronic density. To visualize molecules, create Gaussian input files and as result summary display, the graphical interface GaussView 5.0 was used.

Several Gaussian input files were created in order to obtain information on different molecular properties. Figure 6 illustrates the general scheme of the steps followed to create Gaussian input files to develop the calculations performed throughout this study.

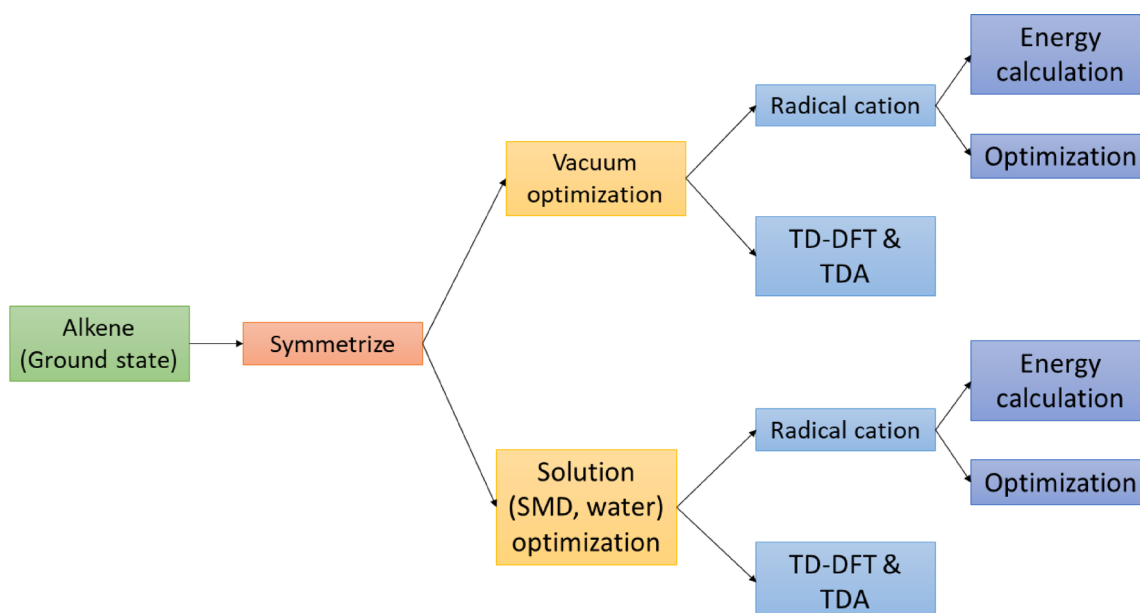


Figure 6. General scheme of the steps followed to create Gaussian input files.

Calculations carried out with the supercomputer were the following: minimization of the molecular structure (optimization + frequency calculation) (first row of table 1), a natural bond order (NBO) analysis (second row of table 1) and the UV-Vis and Raman spectrum calculations (rows 3 and 4 of table 1, respectively). Table 1 summarises the set up submitted in Gaussian to run the calculations. These were applied to the three molecules studied and their corresponding radical cations. Furthermore, D_{2h} symmetry was imposed on ethylene and TME molecules (they originally had C_{2h} and C_1 symmetries, respectively) with the Gaussian tool “symmetrize” and their calculations were performed both in vacuum and in aqueous solution.

Density functional theory (DFT)

Computational chemistry (CC) is based on applying the fundamental laws of quantum mechanics to predict energies and properties of atoms and molecules, approximation methods need to be used to overcome the very complex mathematical equations that are involved.¹⁴ The most important CC methods can be classified in four different families: Empirical Molecular Modelling, Semi-Empirical, *Ab Initio* (of which Hartree-Fock, HF, is the most basic) and Density Functional Theory (DFT), the last three families base their calculations on quantum mechanics.¹⁵ For this research the DFT methods family was selected.

DFT simulation methods are the most popular in CC, its main advantage is that they base their calculations in terms of an observable magnitude, the electronic density ρ , and the energy is expressed as a functional of the density, $E[\rho]$. Although DFT methods are faster and more accurate than *Ab Initio* methods they have a disadvantage: the analytical form of the exchange-correlation functional, $E_{xc}[\rho]$, which is a component of the functional $E[\rho]$, is unknown, which gives rise to a very large number of DFT methods. In this study, the functional selected was B3LYP, which is very useful to simulate carbon compounds.^{14,15}

Time-dependent Density Functional Theory (TD-DFT)

When calculating UV-Vis spectra, DFT should be transformed to take into account that electromagnetic waves have a time-dependent nature. This leads to Time-Dependent Density Functional Theory (TD-DFT), which allows treating excited systems.¹⁶

Table 1. Gaussian calculation setup for the different calculations submitted.

Calculation	Job type	Method				NBO
		Electronic state	Method family	Method	Basis set	
Optimization + frequency	Optimization	Ground State	DFT	B3LYP	6-311G	None
NBO analysis	Energy	Ground State	DFT	B3LYP	6-311G	Full NBO
UV-Vis spectrum	Energy	TD-SCF*	DFT	B3LYP	6-311G	None
Raman spectrum	Frequency**	Ground State				None

*Solve for more states, N = 20; State of interest, Root = 1.

**Compute Raman: Yes; Compute ROA: No; Read Incident Light Freq: Default.

Calculation	Solvation		Closed/open shell	Charge	Spin	Applied molecules
	Model	Solvent				
All of them	None		Default spin	0	Singlet	All neutral species
			Unrestricted	1	Doublet	All radical cations
	SMD	Water	Default spin	0	Singlet	All neutral species
			Unrestricted	1	Doublet	All radical cations

Modelling open shell systems

Closed shell systems have an even number of electrons divided into pairs of electrons with opposite spin. Calculations on this type of systems use a spin restricted model which considers that the pairs of electrons of opposite spin occupy the same spatial orbital. On the other hand, open shell systems have a different number of spin up (α) and spin down (β) electrons. There are two types of calculations on this type of systems: those in which pairs of electrons of opposite sign are forced to occupy the same spatial orbital (spin restricted open model) and those in which spin up and spin down electrons are allowed to occupy different spatial orbitals, called α and β orbitals (spin unrestricted model).^{14,17} In figure 7 the different methods described are represented.

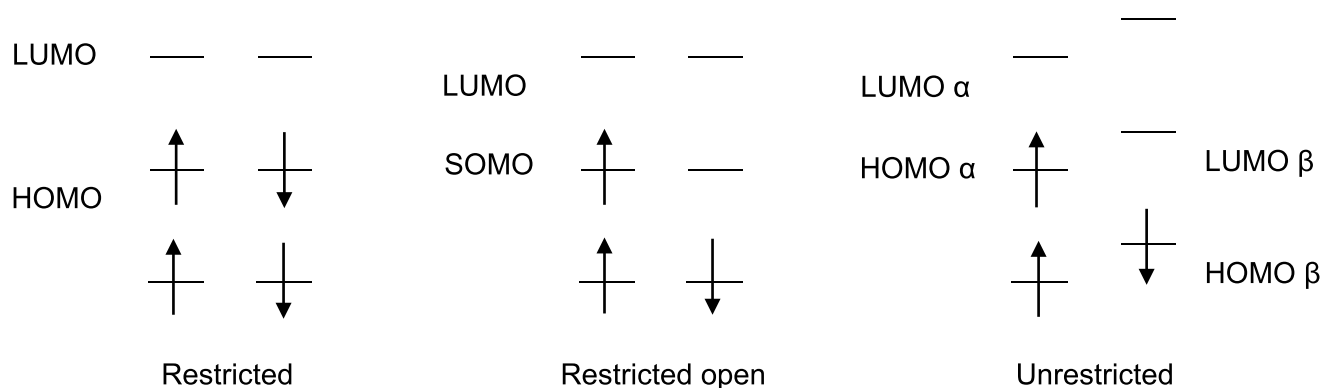


Figure 7. Difference between spin restricted, restricted-open and unrestricted models.

Unrestricted model calculations usually give lower energies and a better description of the unpaired electron density distribution, but its wavefunction is not an eigenfunction of the $\langle S^2 \rangle$ operator. As a consequence, the wavefunction can get deviated from the real one, particularly for spin-delocalized systems such as the radical cations of the molecules studied. The degree of deviation can be obtained comparing the $S(S+1)$ value of the system and the expected one for a doublet state, which is 0.75 (in a doublet state $S = 0.5$). If the value for $S(S+1)$ obtained is close to 0.75 the unrestricted model is well applied to that system.¹⁷

Solvation calculations: SMD Method

A significant part of chemical processes take place in solution, for that reason, the effect of the solvent was measured in the studied molecules. Solvation models used in Gaussian belong to the family of Self-Consistent Reaction Field (SCRF) methods, which are characterized by the following statements: the solvent is considered a continuous and uniform dielectric medium of dielectric constant ϵ , the solute is modelled as a single molecule in a very diluted solution and it's located on an empty cavity in the solvent dielectric medium experiencing electrostatic interactions with it, i.e. the solute and the solvent mutually polarize each other.¹⁴

In this study, a continuum solvation model called SMD (solvation model based on density) was used to develop the solvation calculations. The model is continuum, that is, the solvent is not considered a set of discrete solvent molecules but a dielectric medium. An advantage of the SMD model is that it can be applied to any solvent for which certain parameters are known, such as dielectric constant, refractive index, bulk surface tension, and acidity and basicity.^{18,19}

The standard-state free energy of solvation (ΔG_s°) consists in the standard-state free energy of transfer from the gas phase to the solution.¹⁹ The SMD model calculates ΔG_s° , which can be used to obtain other thermodynamic properties in solution, like the relative solubility of a given solute. To accomplish that, the model separates ΔG_s° in two components: the bulk-electrostatic contribution, derived from a SCRF treatment, and the short-range interactions between solute and solvent molecules in the first solvation shell.¹⁸

Natural Bond Orbital analysis (NBO)

The NBO analysis performed was focused on second-order perturbative estimations of donor-acceptor interactions. In this analysis all possible interactions between filled Lewis-type NBOs (donors) and empty non-Lewis NBOs (acceptors) are analysed, these interactions, which lead to deviations from the Lewis structure, are called delocalization corrections to the zeroth-order natural Lewis structure. For each donor NBO and acceptor NBO, the stabilization energy associated with delocalization is estimated by 2nd-order perturbation theory. Interactions are recorded only when the interaction energy exceeds 0.5 kcal/mol.²⁰

Theoretical determination of reduction potential

Computational methods used to predict reduction potentials can be classified in two types: direct method and indirect method. The first one directly calculates the reduction potential from the solvated oxidized and reduced forms of the involved species while the second one takes into account its thermodynamic cycle. Although the indirect method gives rise to more accurate results, its theoretical complexity led to the use of direct method in this study.²¹

Results and discussion

Molecules were studied at a temperature of 298.150 K and a pressure of 1 atm (standard conditions). In all the radical cations it was obtained a value of $S(S+1)$ close to de desired one of 0.750, so the spin unrestricted model worked properly.

Thermochemistry

Standard Gibbs free energy and symmetry point group for each molecule were obtained and represented in table 2.

Table 2. Symmetry and Gibbs free energy obtained for the studied molecules.

Molecule		Symmetry	G^0 (kJ/mol)		
Ethylene	Non symmetrized	Vacuum	Neutral	C_{2h}	$-2,06 \cdot 10^5$
			Radical cation	C_2	$-2,05 \cdot 10^5$
	Symmetrized	Vacuum	Neutral	D_{2h}	$-2,06 \cdot 10^5$
			Radical cation	D_2	$-2,05 \cdot 10^5$
		Aqueous solution	Neutral	D_{2h}	$-2,06 \cdot 10^5$
			Radical cation	D_2	$-2,06 \cdot 10^5$
TME	Non symmetrized	Vacuum	Neutral	C_1	$-6,19 \cdot 10^5$
			Radical cation	C_1	$-6,18 \cdot 10^5$
	Symmetrized	Vacuum	Neutral	D_{2h}	$-6,19 \cdot 10^5$
			Radical cation	C_1	$-6,18 \cdot 10^5$
		Aqueous solution	Neutral	D_2	$-6,19 \cdot 10^5$
			Radical cation	C_1	$-6,19 \cdot 10^5$

TMOE	Non symmetrized	Vacuum	Neutral	C ₁	-1,41·10 ⁶
			Radical cation	C ₁	-1,41·10 ⁶
		Aqueous	Neutral	C ₁	-1,41·10 ⁶
		solution	Radical cation	C ₁	-1,41·10 ⁶

In table 2 it can be observed that ethylene is the least stable species (it has the highest value of G^0) because it doesn't have stabilization of the double bond by inductive effects such as TME and TMOE. On the other hand, TMOE radical cation has a significantly lower value of G^0 than the other species, which leads to think that methoxy substituents can stabilize considerably well the double bond.

In order to give a comparison of the obtained results, G^0 of symmetrized and non-symmetrized ethylene and TME, vacuum and aqueous solution molecules and neutral and radical cation were subtracted and collected in table 3.

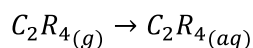
Table 3. Comparison between Gibbs free energies.

		Ethylene	TME	TMOE
ΔG^0 (non-symmetrized - symmetrized); kJ/mol	Neutral	-1,72	-2,95	-
	Radical cation	-1,72	0,00	-
ΔG^0 (aqueous solution - vacuum); kJ/mol	Neutral	5,16	8,81	16,59
	Radical cation	-300,35	-229,31	-201,44
ΔG^0 (radical cation - neutral); kJ/mol	Vacuum	990,25	760,20	659,36
	Aq solution	684,74	522,08	441,33

The first comparison was performed between symmetrized and non-symmetrized species. As it can be seen in table 3, although the Gibbs free energy is lower in C_{2h} ethylene than in D_{2h} ethylene, in C₂ ethylene radical cation than in D₂ ethylene radical cation and in C₁ TME than in D_{2h} TME, which means that non-symmetrized species are more stable. The difference is so small that just D_{2h} ethylene and TME and D₂ ethylene radical cation will be considered in this study, which is the real symmetry of the species. In TME radical cation a value of 0 was obtained because in the symmetrized molecule

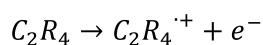
C_1 was the symmetry attained, which matches with the symmetry of the non-symmetrized molecule.

ΔG when changing from vacuum to aqueous solution represents the Gibbs free energy involved in the solvation process (ΔG_s^0):



where $R = H, CH_3, OCH_3$. In neutral molecules ΔG_s^0 values are not large and positive, so G^0 is lower in vacuum than in aqueous solution. ΔG_s^0 increases from ethylene to TMOE, so in neutral species solvation is not thermodynamically favourable, water destabilizes slightly the molecule and that destabilization is more important in TMOE. In radical cations ΔG_s^0 is larger and negative, so G^0 is lower in aqueous solution than in vacuum. ΔG_s^0 absolute value increases from TMOE to ethylene, so in this case solvation of radical cations is thermodynamically favourable, water molecules stabilize the radical cation and that stabilization is more important in ethylene.

When comparing between neutral species and radical cations, ΔG^0 value represents the Gibbs free energy involved in the reaction:



Values obtained are high and positive, which means that the reaction is not thermodynamically favourable, so that, radical cations are significantly less stable than neutral parents. This destabilization is more important in ethylene and in vacuum, and is less important in TMOE and in aqueous solution, *i.e.* solvation stabilizes the radical cation. In TME and TMOE, stabilization of the radical cation by inductive effects is more important than in ethylene, which has the highest ΔG^0 value, due to the increment in the number of substituents in the molecule; furthermore, in TMOE, with the lowest ΔG^0 value, the oxygen exerts an increment in the stabilization, which can take place by resonance (Fig. 8).

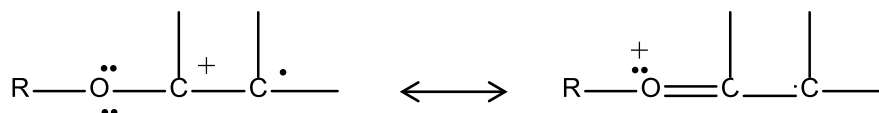
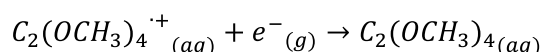
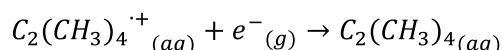
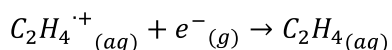


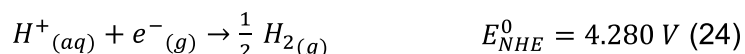
Figure 8. Resonance forms of radical cation with a methoxy substituent.

This can help to understand why ΔG_s^0 is lower in ethylene radical cation and higher in TMOE radical cation, it makes sense that the strongest stabilization takes place in the more destabilized species.

From the Gibbs Free Energy another relevant magnitude can be obtained: the reduction potential. Redox half reactions for the three compounds in aqueous solution are:



with the thermodynamic relationship $\Delta_{red}G^0 = -nFE_{abs}^0$ where E_{abs}^0 is the absolute standard redox potential, $\Delta_{red}G^0$ is the standard Gibbs free energy for the reduction reaction F is the Faraday constant $F = 96485.332 \text{ C/mol}$ and n is the number of electrons involved in the reaction, in this case $n = 1$, E_{abs}^0 can be calculated. Experimental redox potentials are obtained with respect to a reference, the most common one is the normal hydrogen electrode (NHE):



Reduction potential respect to this reference electrode can be obtained subtracting the value for the E_{NHE}^0 to the absolute redox potential calculated. Results obtained are shown in table 4.

Table 4. Obtention of the absolute and relative redox potentials of the studied molecules.

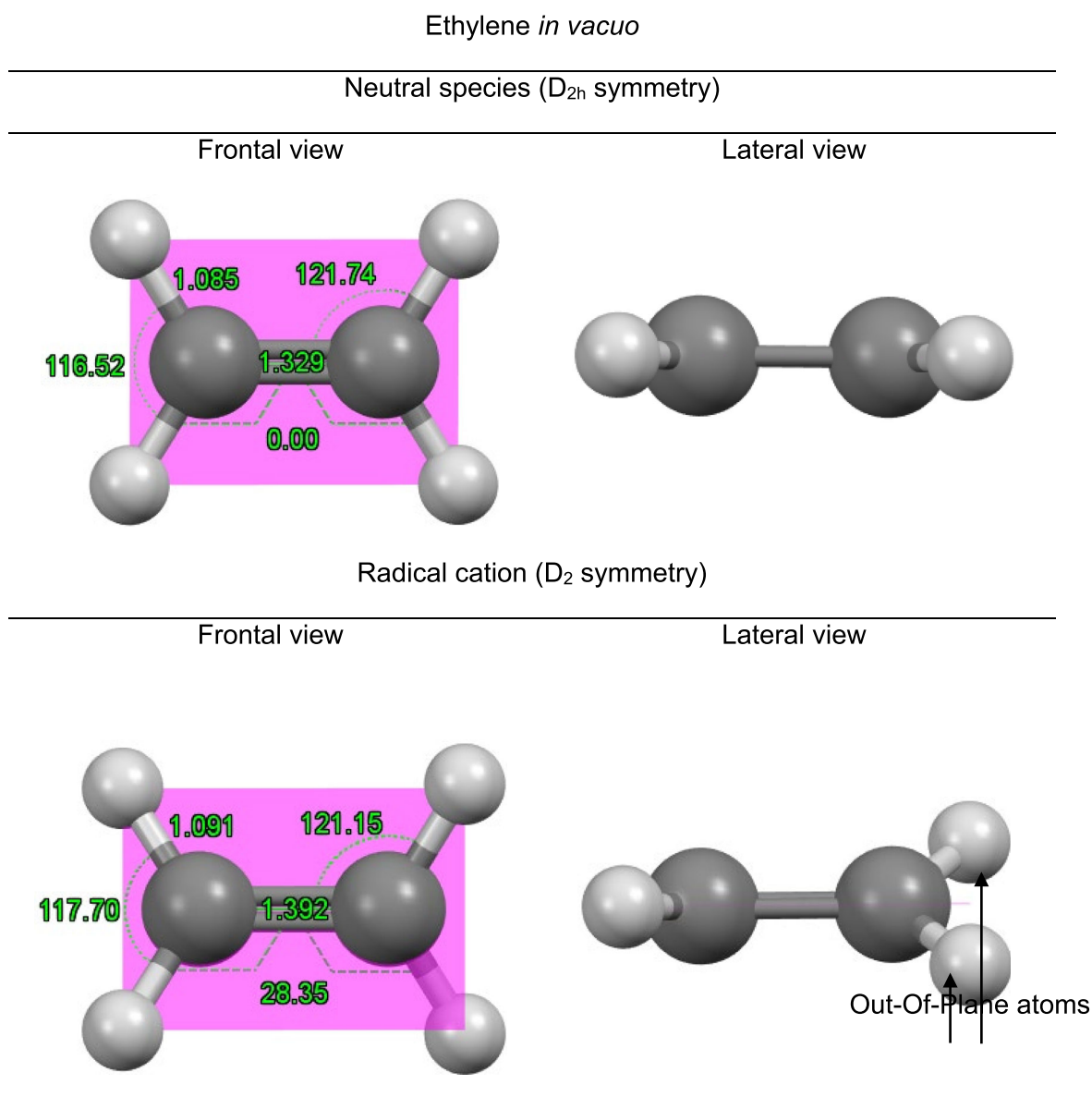
	$\Delta_{red}G^0$ (J/mol)	E_{abs}^0 (V)	$E_{ref(NHE)}^0$
Ethylene	$-6,85 \cdot 10^5$	7,10	2,82
TME	$-5,22 \cdot 10^5$	5,41	1,13
TMOE	$-4,41 \cdot 10^5$	4,57	0,29

Values obtained are reasonable. The highest redox potential obtained is for ethylene and the lowest is for TMOE. All reduction reactions are thermodynamically favourable as the radical cation is always less stable than the neutral species. The reduction potential is higher when the radical cation is less stable.

Angles and bond distances

Bond distances obtained for each molecule as well as angles and dihedral angles and the symmetry of the molecule are shown in table 5:

Table 5. Geometry of studied molecules.

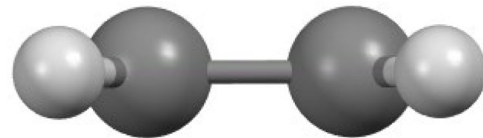
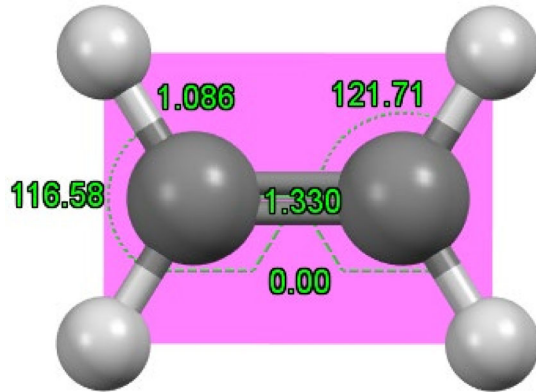


Ethylene in aqueous solution

Neutral species (D_{2h} symmetry)

Frontal view

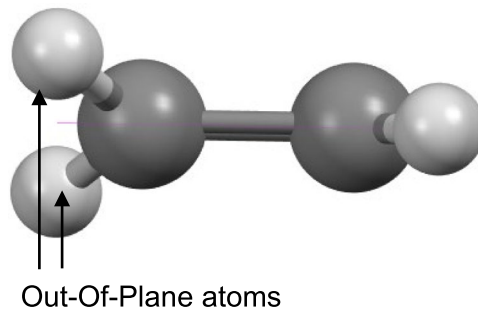
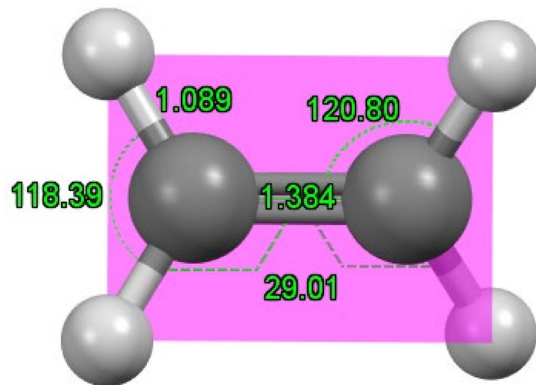
Lateral view



Radical cation (D_2 symmetry)

Frontal view

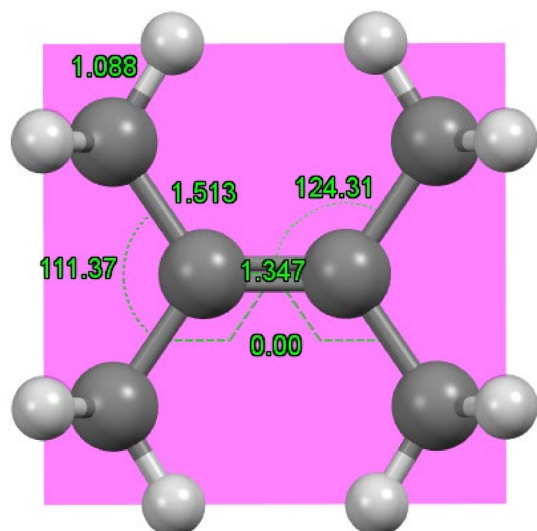
Lateral view



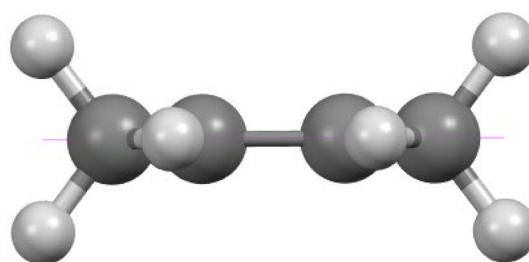
TME *in vacuo*

Neutral species (D_{2h} symmetry)

Frontal view

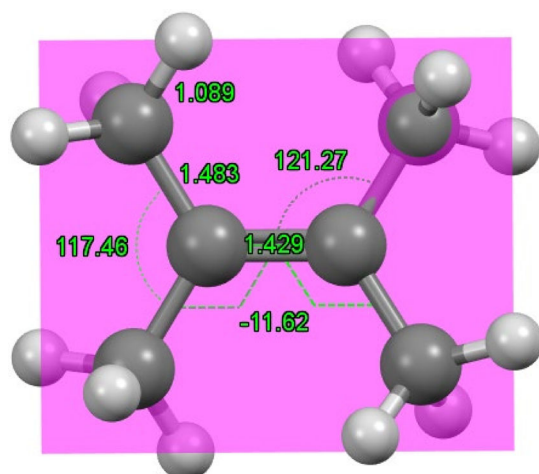


Lateral view

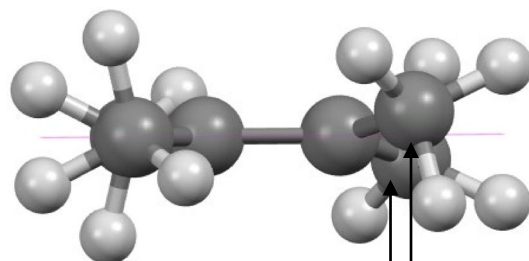


Radical cation (C_1 symmetry)

Frontal view



Lateral view

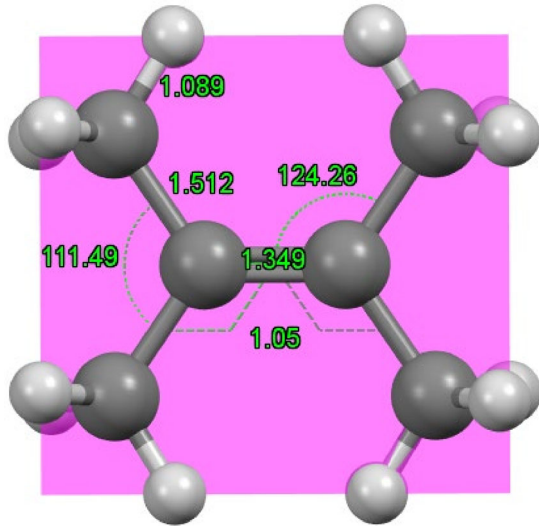


Out-Of-Plane atoms

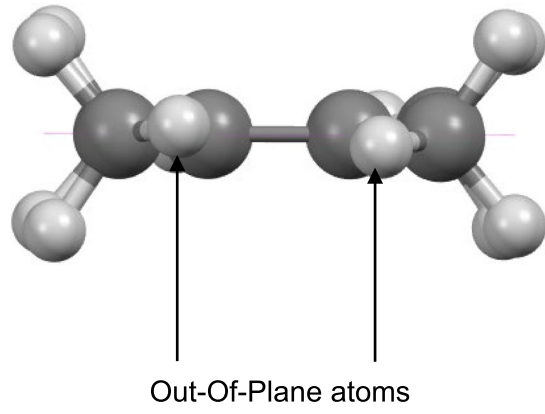
TME in aqueous solution

Neutral species (D_2 symmetry)

Frontal view

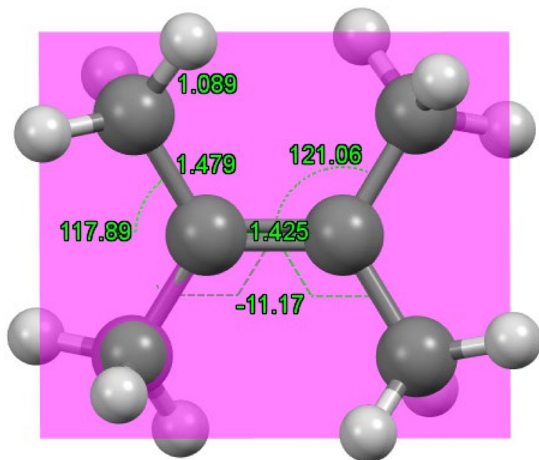


Lateral view

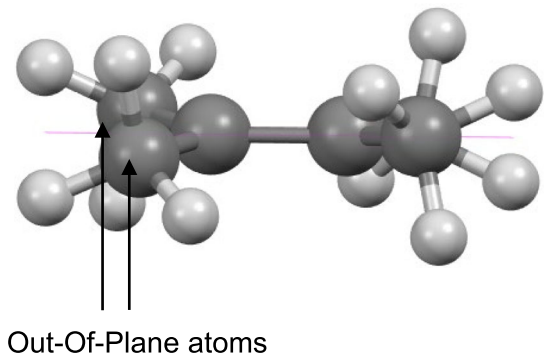


Radical cation (C_1 symmetry)

Frontal view



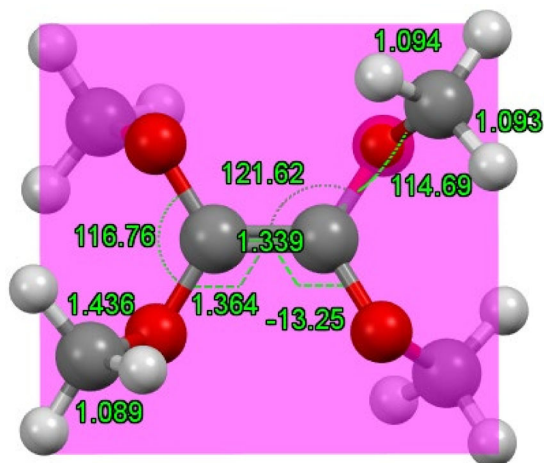
Lateral view



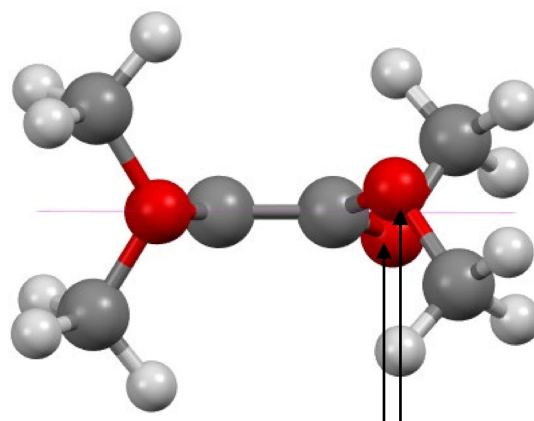
TMOE *in vacuo*

Neutral species (C_1 symmetry)

Frontal view



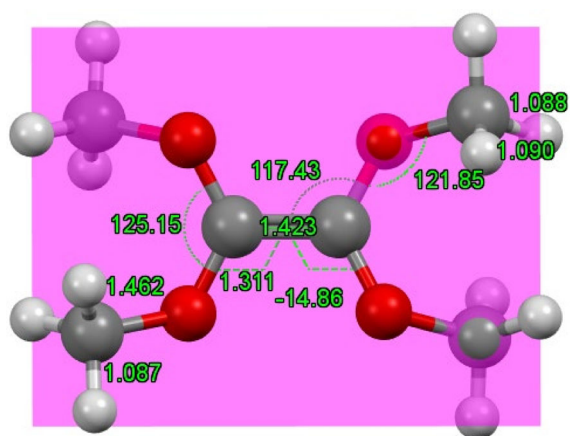
Lateral view



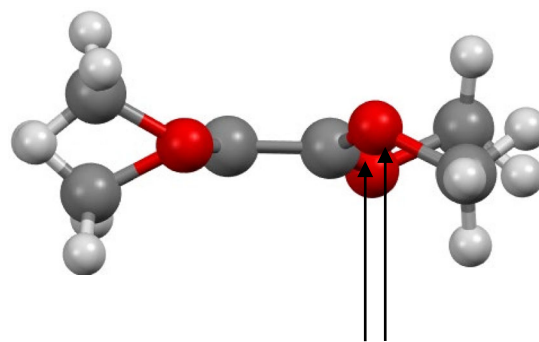
Out-Of-Plane atoms

Radical cation (C_1 symmetry)

Frontal view



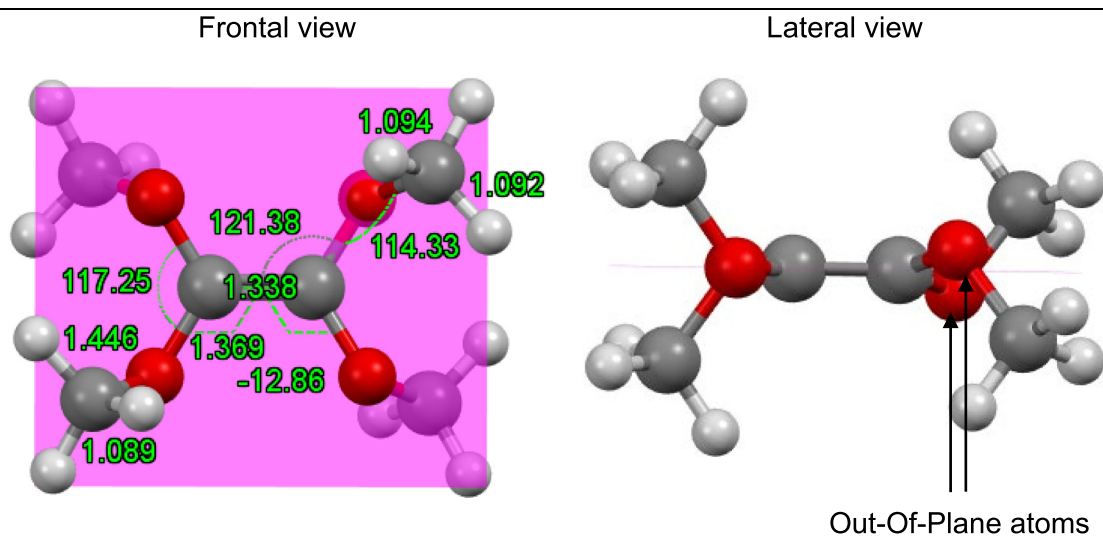
Lateral view



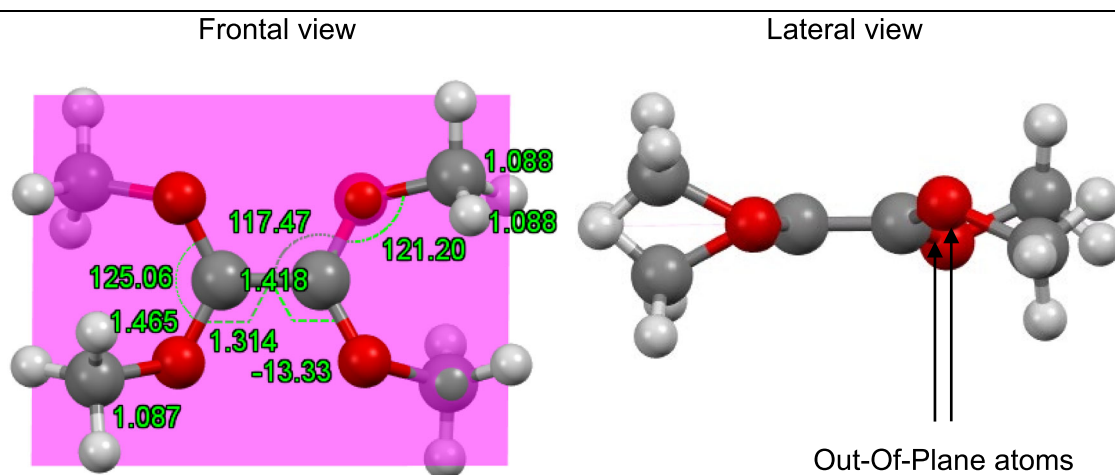
Out-Of-Plane atoms

TMOE in aqueous solution

Neutral species (C_1 symmetry)



Radical cation (C_1 symmetry)



As a general trend, the molecular arrangement changes when it switches between the neutral radical and the radical cation, with a reduction of symmetry. Symmetry is higher in ethylene and lower in TMOE. Furthermore, symmetry also undergoes reduction when TME changes from vacuum to aqueous media.

When the radical cation is formed C-C bond distance increases, this is because the neutral molecule has a C-C bond of order 2, which is quite strong, while the radical cation is a conjugated system (Fig. 9) with an average C-C bond order of 1.5, which is weaker than the previous one. That will make the C-C distance larger.

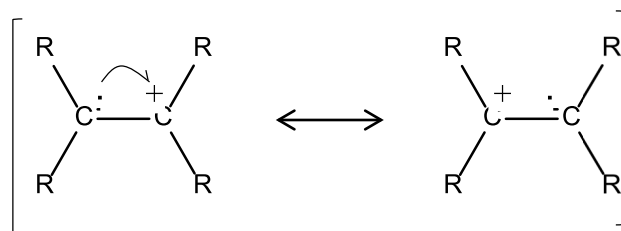


Figure 9. Resonance hybrids of the radical cations. R = H, CH₃, OCH₃

The increment in the C-C bond distance can also be described in terms of the MO theory. This will be explained with ethylene because it's the simplest molecule, but that explanation can be extrapolated to all of them. Looking at ethylene MO diagram in Fig. 4, it can be observed that the highest occupied MO (HOMO) corresponds with a π bonding orbital, to decrease the population in a bonding orbital, as happens in the radical cation, which has had an electron removed, weakens the bond. MO theory describes the bond order as:

$$BO = \frac{1}{2}(e_b - e_a)$$

where e_b is the number of electrons in bonding orbitals and e_a is the number of electrons in antibonding orbitals. Bond order can be calculated in ethylene neutral species and in ethylene radical cation:

$$BO_{C_2H_4} = \frac{1}{2}(8 - 4) = 2$$

$$BO_{C_2H_4^{\cdot+}} = \frac{1}{2}(7 - 4) = 1.5$$

The bond order calculated with the MO theory matches with the bond order calculated with the Lewis structures. The increase in the C-C bond distance can therefore be rationalized as the decrease in the population in a bonding orbital, which weakens the bond.

When changing from vacuum to aqueous media no significant change is observed in the C-C bond distance of the neutral species, but in the radical cation it's observed a reduction. Water is a polar molecule and it will solvate the radical cation orientating its negative pole (the oxygen) towards it; this is, a region rich in electron density will be close to the radical cation. That can increase slightly the population in the bonding HOMO orbital of it, which will strength the C-C bond, thus reducing its distance.

Looking at the C-H distance of ethylene, for the neutral species in vacuum and in aqueous solution no significant change is observed. On the other hand, an increment in the C-H distance is observed in the radical cation in vacuum. When the radical cation is formed, the carbon atoms of the molecule have lack of electronic density as the positive charge is shared between them. Part of the electronic density of the C-H bond will be displaced towards the C atoms to compensate the lack of negative charge. That can weaken the C-H bond making its distance larger. In aqueous media, this effect gets attenuated where it can be observed that the enlargement of the C-H distance is not very important, probably this is because of the stabilization of the radical cation by water molecules.

In TME and TMOE the opposite effect is observed. In TME the distance C-CH₃ decreases and that effect gets incremented in aqueous solution. No significant change is observed in the C-H distance. In TMOE the distance C-OCH₃ gets significantly diminished and in aqueous solution the same effect is observed with similar distance values for both species. This can be explained with the resonant forms that stabilize the radical cation in TMOE that are represented in Fig. 6, where oxygen donates part of its electron density to the C-OCH₃ bond, introducing a contribution of double bond on it that makes it stronger. It's observed that O-CH₃ distance increases, the donation of electronic density to the C-OCH₃ bond strengthens that bond, but weakens the O-CH₃ one. In aqueous solution, the O-CH₃ bond distance of the neutral species increases quite a bit, maybe because a kind of H-bond is established between the oxygen and water, which weakens the O-CH₃ bond. In the radical cation it increases very little, it can be because oxygen is already donating charge to the C, and, thus, the formed H-bond is not so strong. C-H distance decrease a bit when the radical cation is formed, but the effect is not significant; furthermore, in TMOE not all of them are equal as in TME.

About the angles, in ethylene H-C-H angles vary very little in the neutral species in vacuum and in aqueous solution, but it increases significantly when the radical cation is formed. An even higher H-C-H angle opening is observed in the radical cation when changing from vacuum to aqueous medium. C-C-H angles are very similar in the neutral molecule in vacuum and in aqueous media and in the radical cation in aqueous media, but it decreases a bit in the radical cation in vacuum. In TME and in TMOE no significant change was found when changing from vacuum to aqueous media. In TME H₃C-C-CH₃ angle increases and C-C-CH₃ angle decreases a bit when the radical cation is formed, while in TMOE O-C-O and C-O-C angles increases and C-C-O angle decreases a bit.

Dihedral angles R-C-C-R where also measured, it was found that in neutral ethylene in

vacuum and in aqueous solution and in neutral TME in vacuum it has a value of 0, which means that those molecules are contained in a plane. For the other species it was found a value different from 0, which indicates that the species is not planar. For neutral TME in aqueous solution a value very close to zero was obtained, indicating that the fold of that molecule is very small. In TMOE a very small change in the dihedral angle was observed from the neutral species to the radical cation.

In conclusion, reduction of the double bond to a single bond, *i.e.* passing from a carbon sp^2 to a carbon sp^3 , makes the species lose the planarity; that will affect its symmetry, which reduces. C-C single bond is not rigid as the C-C double bond, so in the radical cation, the C-C bond can rotate and different conformations can take place. Moreover, the loss planarity also introduces steric hindrance that makes the C-C bond less accessible.

NBO analysis

Donor-acceptor interactions in the NBO analysis were studied to understand better the bonding in the studied species. In table 6 the most important delocalizations are collected with the donor NBO and acceptor NBO involved in the interaction and the stabilization energies attained. Important delocalizations only were found in TMOE.

From this analysis it can be concluded that in TMOE, oxygen certainly donates electronic density to central carbon atoms of the molecule. In the neutral molecule in vacuum there is donation from the lone pairs of two oxygen atoms to the antibonding C-C bond, but that delocalization is not so important; there is an important transfer of electronic density from the first C-C antibonding orbital to the second one. In aqueous solution those delocalizations in the neutral molecule are not important.

In the radical cation in vacuum only significant delocalizations of the β spin orbitals are found, which are from the lone pair of the four oxygen atoms to the central carbon atoms, and the delocalization between C-C antibonding orbitals present in the neutral species in vacuum is not important. In aqueous solution delocalizations of α spin orbitals take place but they are not very significant, they all consist in donations from the lone pairs of the four oxygen atoms to the C-C antibonding orbital; in β spin orbitals more important delocalizations take place, they are from the lone pairs of the four oxygen atoms to the central carbon atoms.

Table 6. Donor-acceptor interactions in the NBO analysis.

Molecule	Donor NBO	Acceptor NBO	E (kcal/mol)
TMOE neutral in vacuum	LP (2) O4	BD*(1) C1-C2	13,50
	LP (2) O6	BD*(1) C1-C2	13,73
	BD*(1) C1-C2	BD*(2) C1-C2	36,75
TMOE radical cation in vacuum (β spin orbitals)	LP (2) O3	LP*(1) C2	42,76
	LP (2) O4	LP*(1) C2	30,67
	LP (2) O5	LP*(1) C1	40,84
	LP (2) O6	LP*(1) C1	32,02
TMOE radical cation in aqueous solution (α spin orbitals)	LP (2) O3	BD*(2) C1-C2	12,80
	LP (2) O4	BD*(2) C1-C2	12,80
	LP (2) O5	BD*(2) C1-C2	12,80
	LP (2) O6	BD*(2) C1-C2	12,80
TMOE radical cation in aqueous solution (β spin orbitals)	LP (2) O3	LP*(1) C2	39,65
	LP (2) O4	LP*(1) C2	39,65
	LP (2) O5	LP*(1) C1	39,65
	LP (2) O6	LP*(1) C1	39,65

In β spin orbitals the same delocalizations in vacuum and in aqueous solution take place but stabilization energies differ. In vacuum stabilization energies from the four delocalizations are different, two are close to 40 kcal/mol and the other two are close to 30 kcal/mol, but in aqueous solution the four have the same value (39.65 kcal/mol). From the delocalizations with energies close to 40 kcal/mol not significant change takes place, but delocalizations close to 30 kcal/mol became more important. This effect in aqueous media of the four delocalizations having the same energy is also observed in α spin orbitals, where a stabilization energy of 12.80 kcal/mol has been found for the four delocalizations. The fact that in aqueous solution stabilization by both α and β spin orbitals became more important can contribute to the fact that radical cation became more stable in aqueous solution than in vacuum.

In conclusion, such high stabilization energies are only found in TMOE, even in its neutral form, where the double bond is stabilized by the oxygen and through a delocalization within the C-C bond, that's the reason why this molecule is the most stable one (it has

the lowest G^0 value). On the other hand, donation from oxygen atoms to central carbon atoms of the molecule is more important in radical cations and it can be concluded that oxygen significantly stabilizes the radical cation by electronic density donation.

In TME, although significant stabilization energies were not found, some delocalizations with a stabilization energy close to 5 kcal/mol were found in the β spin orbitals from radical cation in vacuum, and in the neutral species in vacuum and in aqueous solution. Delocalizations in the radical cation are from C-H bonding orbitals to central carbon atoms and delocalizations in the neutral molecule, both in vacuum and in aqueous solution, are from C-CH₃ bonding orbitals to C-CH₃ antibonding orbitals in the trans position.

This last can explain why in the neutral molecule a higher C-CH₃ distance than in the radical cation was found, because the change of electronic density from bonding orbitals to antibonding orbitals weakens the C-CH₃ bond in the neutral species, effect that does no longer takes place in the radical cation. The stabilization energy of this delocalization is similar in vacuum and in aqueous solution, this matches with the previous observation that C-CH₃ distance didn't change so much in vacuum and in aqueous solution.

It's found that delocalizations of oxygen in TMOE radical cation are much more important than this delocalization of the C-CH₃ bond in neutral TME, that's the reason why a higher difference in the C-O distance between TMOE neutral species and radical cation than in the C-CH₃ distance between TME neutral species and radical cation is attained.

In ethylene no important delocalizations were found neither in neutral species nor in radical cation. This agrees with the fact that H substituents capacity to delocalize is very limited as well as its capacity to stabilize the radical cation. That's the reason why ethylene is the least stable species (it has the highest G^0), because H is not able to stabilize the double bond, and why ethylene radical cation is also the most destabilized (it has the highest ΔG^0 (radical cation - neutral)), because H cannot stabilize the radical cation.

Vibrations

IR and Raman spectra were obtained and represented in the same plot. Here are only collected the ethylene ones, whereas TME and TMOE spectra are collected in the annex.

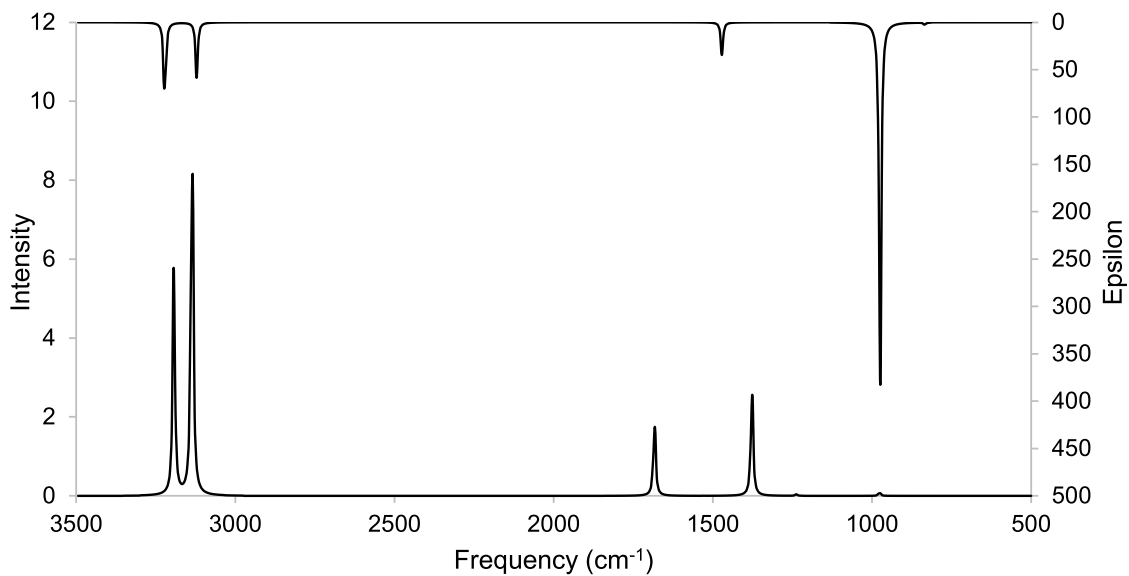


Figure 10. IR and Raman spectra of ethylene in vacuum

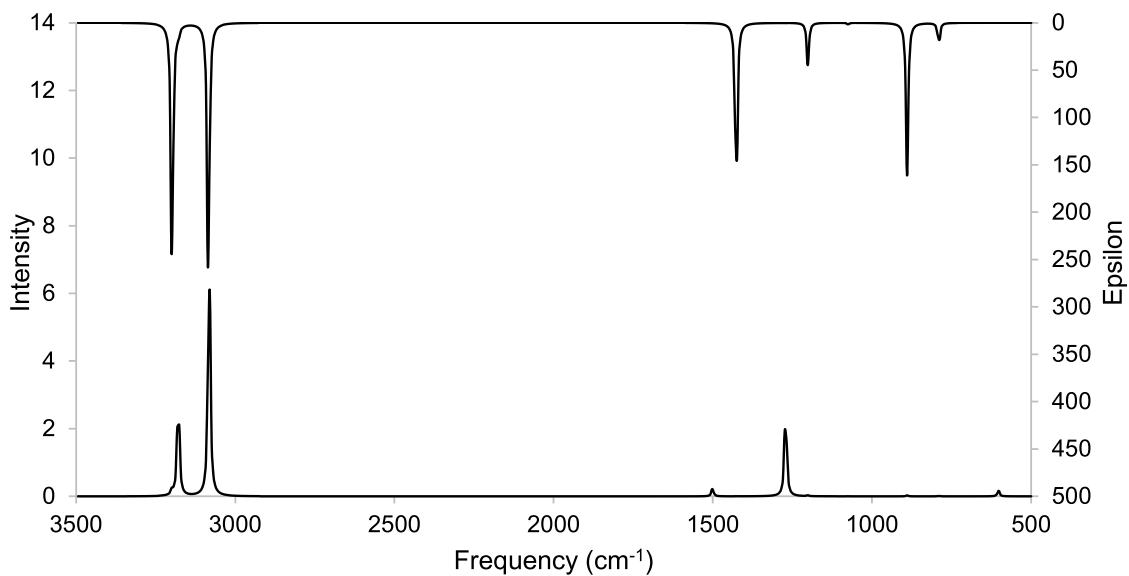


Figure 11. IR and Raman spectra of ethylene radical cation in vacuum

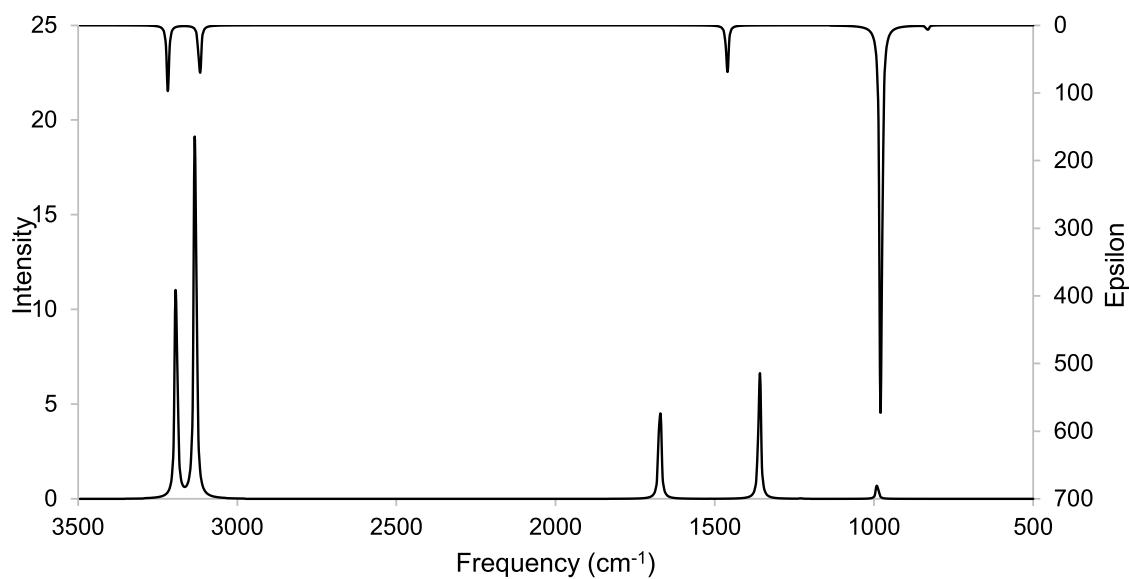


Figure 12. IR and Raman spectra of ethylene in aqueous solution

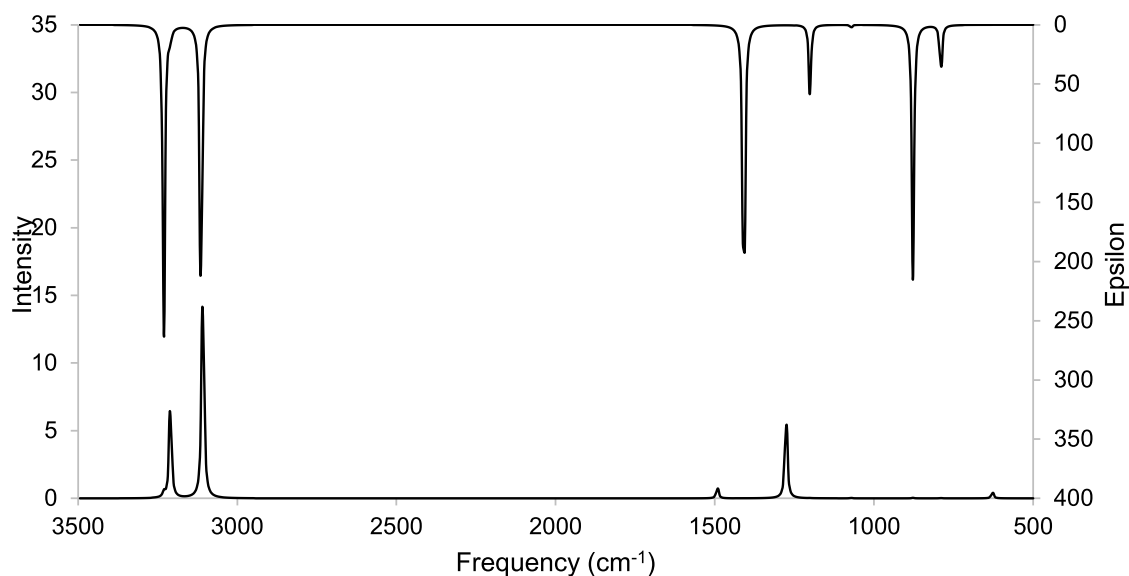


Figure 13. IR and Raman spectra of ethylene radical cation in aqueous solution

In neutral ethylene and in TME in vacuum, molecules which have D_{2h} symmetry, it can be observed that the rule of mutual exclusion is fulfilled as those molecules have a center of symmetry, so normal modes active in Infrared are not active in Raman and vice-versa. Radical cations, as seen, suffer a decrease in symmetry and they do not possess a center of symmetry, so this rule is not satisfied; neutral TMOE and TME in aqueous solution neither have a center of symmetry and the rule in them is not fulfilled.

It's known that the number of vibration modes follows the equation $3N-6$ for non-linear molecules (being N the number of atoms in the molecule), so it's expected that as the number of atoms in the molecule increases a higher number of bands appear in the spectrum, this is what is observed when comparing the spectra of the three molecules. Those modes can be degenerated in energy, degenerations more likely appear in systems with a higher symmetry, so it's expected that as the symmetry decreases and a higher number of bands appear in the spectrum. In ethylene spectra this can be observed as in the radical cation spectrum a higher number of bands is observed; in TME this effect can also be observed, even more clear, but in TMOE, as the number of bands in the spectrum is quite high and most of them have a very low intensity and are not appreciated in the spectrum, the effect is harder to see.

In ethylene, in general it can be observed that vibration modes frequencies are higher in the neutral molecule than in the radical cation. This can better be seen in table 10 of the annex, where the subtraction of the vibration frequency for a given vibration mode of the neutral molecule to that of the radical cation was calculated. In general, at higher bond strengths, higher vibrational frequencies are reached, that's the case in ethylene, as it was seen in the radical cation C-C bond gets weaker, so vibrational modes shift to lower frequencies. On the other hand, for TME and TMOE that tendency is not so clear and they were found values that shifted to lower frequencies but also values that shifted to higher frequencies. This can be because, as it was seen in NBO analysis, in those species the bond is more complex and there are other contributions that can affect to the strength of the bond.

When comparing spectra in vacuum and in aqueous media it can be observed that higher intensities are attained in the spectrum peaks and a change in their shift is observed, but not a clear tendency towards the increase or the reduction in vibrational frequencies can be established. Table 11 of the annex shows the difference between vibration frequencies in vacuum and in aqueous solution for all the species. In Fig. 14 the difference in vibrational frequency of the neutral species and the radical cation in vacuum vs in aqueous solution is represented for ethylene, TME and TMOE. It's observed that a linear relationship is followed by the three compounds with a slope close to 1 for all of them, which means that when changing from the neutral species to the radical cation a similar displacement in the vibrational frequency takes place in vacuum and in aqueous solution.

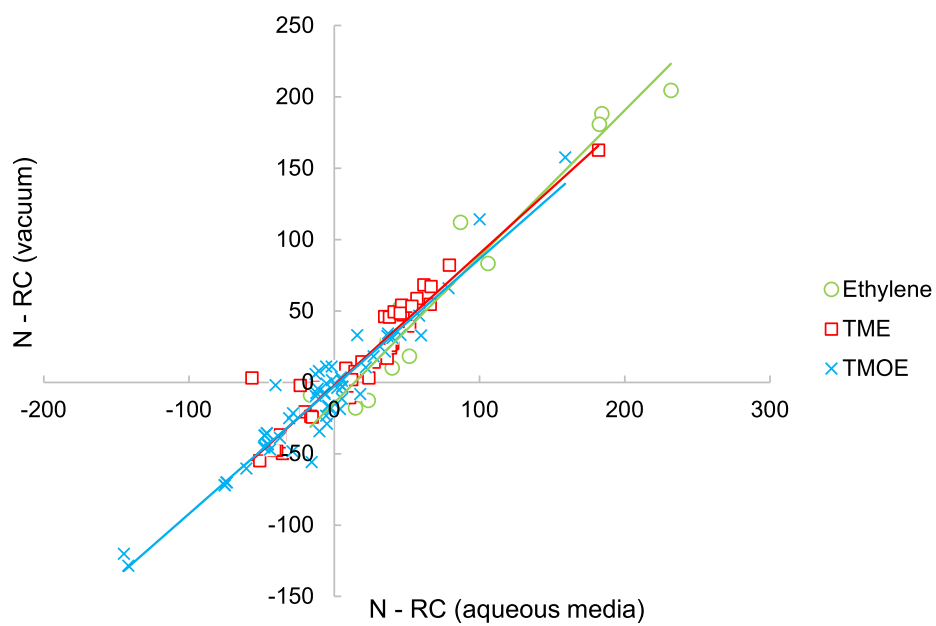
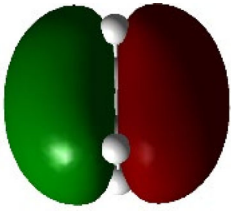
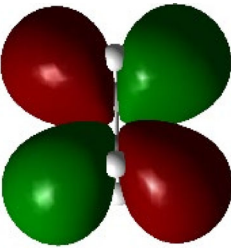
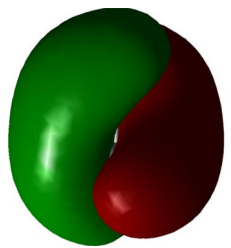
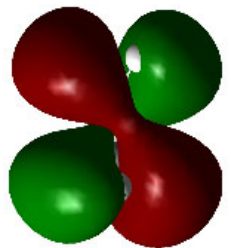
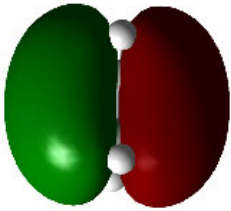
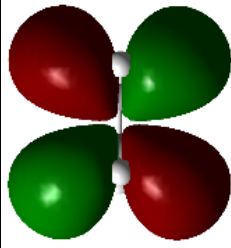
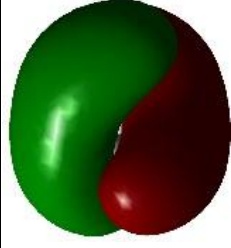



Figure 14. Relationship between vibration differences in vacuum and aqueous solution

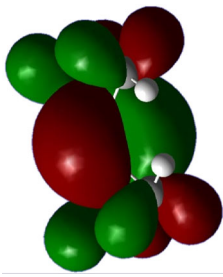
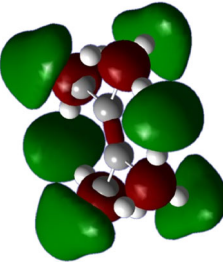
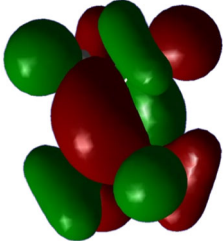
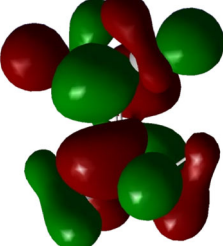
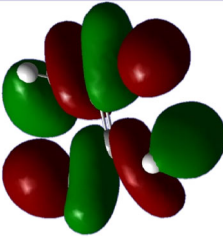
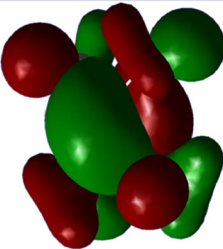
Molecular Orbitals

HOMO and LUMO obtained for the studied species are collected next. For radical cations they are separated in α spin orbitals and β spin orbitals. Table 7 shows the results obtained.

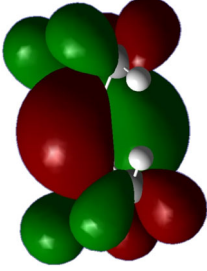
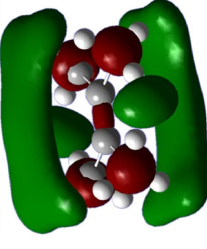
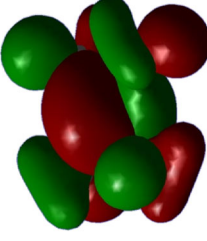
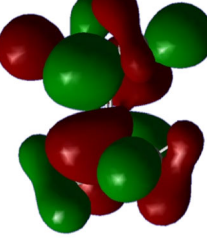
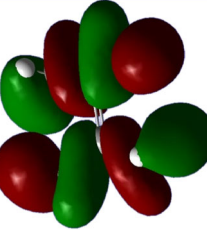
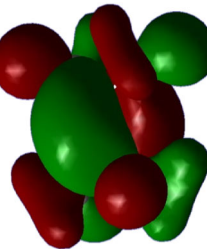
Table 7. MOs obtained for the studied molecules.

		Ethylene <i>in vacuo</i>		
		Neutral species		Radical cation
Orbital Type	HOMO	LUMO	HOMO α	LUMO α
Orbital Number	8	9	8	9
MO Representation				
E (Hartrees)	-0.28149	-0.01084	-0.59476	-0.35163
			-0.67448	-0.46667
		Ethylene in aqueous solution		
MO Representation				
E (Hartrees)	-0.28023	-0.00871	-0.36141	-0.11926
			-0.44233	-0.23420

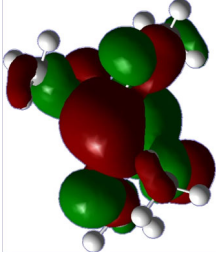
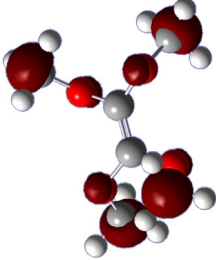
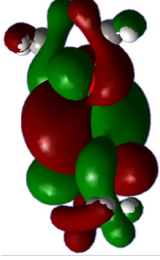
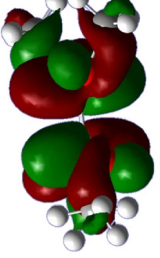
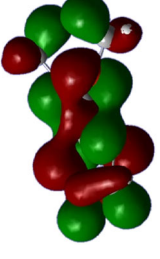
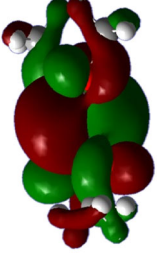
TME *in vacuo*

Neutral species		Radical cation				
OT	HOMO	LUMO	HOMO α	LUMO α	HOMO β	LUMO β
ON	24	25	24	25	23	24
MO						
E (Ha)	-0.22722	-0.01016	-0.45375	-0.23841	-0.54157	-0.35599

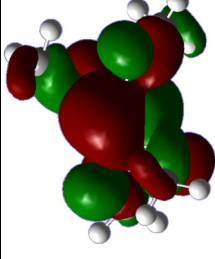
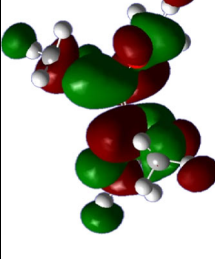
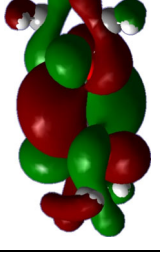
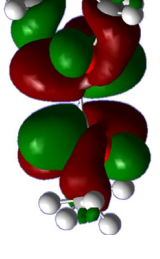
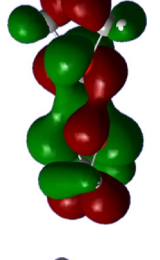
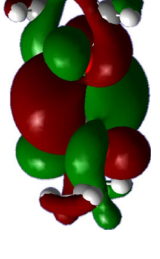
TME in aqueous solution

MO						
E (Ha)	-0.22410	-0.00374	-0.27716	-0.06156	-0.36785	-0.17819

TMOE *in vacuo*

Neutral species		Radical cation				
OT	HOMO	LUMO	HOMO α	LUMO α	HOMO β	LUMO β
ON	40	41	40	41	39	40
MO						
E (Ha)	-0.21618	-0.00698	-0.36838	-0.16212	-0.47908	-0.28063

TMOE in aqueous solution

MO						
E (Ha)	-0.21728	-0.03035	-0.22370	-0.01627	-0.33397	-0.13539

Making a comparison of the MO energies of the neutral species and the radical cation it is observed that when the radical cation is formed, the MO energy diminishes. This can be rationalized with a very basic formula for the potential energy that feels an electron to the nucleus:

$$U = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Where ϵ_0 is the vacuum permittivity, e is the charge of the electron, Z is the atomic number and r is the distance of the electron to the nucleus. Attending to that formula, when the potential energy decreases it should be because the radius decreases too, as the other magnitudes are not changing in the same molecule. Therefore, in the radical cation, electrons are closer to the nucleus and are linked stronger to it. This can be rationalized as: the second ionization potential of the molecule is higher than the first one because, when an electron is ejected, the effective nuclear charge is higher.

In the radical cations a slight increment in MO energy is observed when changing from vacuum to aqueous solution. This is related with the fact that water stabilizes the radical cation, already commented before because if the radical cation is in a more stable state, it will not be so hard to remove another electron from it. In neutral ethylene and TME a slight increment in MO energies in aqueous media takes place, so solvation stabilizes a bit those molecules, but in TMOE the opposite is observed, in aqueous solution energy of MO diminishes slightly, so solvation should destabilize a bit the molecule. Looking at the NBO analysis it was observed that in neutral TMOE in vacuum some delocalizations with quite high stabilization energy took place which in aqueous media were not important, that lack of delocalizations in aqueous media can be the reason why solvation destabilizes the molecule.

Within the radical cation MO it is observed that the energy of the α spin MO is lower than the β spin MO, for orbitals with the same orbital number, as it was described in Fig. 7.

When the radical cation is formed, a great difference in the shape and in the symmetry of the MO is observed, the highest difference is found between the 41 and 41 α orbitals of the TMOE. On the other hand, in MO shape of the species in vacuum and in aqueous media, not a high difference is observed, although a relevant change occurs in the LUMO of neutral TMOE. Furthermore, in TME, HOMO α and LUMO β , which have the same orbital number, have the same shape but opposite sign, while in ethylene and TMOE no significant difference is observed between them.

Accordinging with Koopmans' theorem, already introduced, ionization potential can be calculated from the negative of the energy of the HOMO. Table 8 shows ionization energies obtained with this method.

Table 8

		Ionization energy (eV)	
		First	Second
Ethylene	Vacuum	7,66	16,18
	Aqueous solution	7,63	9,83
TME	Vacuum	6,18	12,35
	Aqueous solution	6,10	7,54
TMOE	Vacuum	5,88	10,02
	Aqueous solution	5,91	6,09

It is observed that the highest ionization energy is found for ethylene as its radical cation is the least stable one, as it was already discussed, and the lowest one for TMOE whose radical cation is the most stabilized. In aqueous solution ionization energies decreases due to the stabilizing effect of the solvation of water molecules, this effect is higher in radical cations, where the stabilization is greater, than in neutral molecules and in neutral TMOE a destabilization instead of a stabilization takes place with solvation. Finally, second ionization energies are always higher than the first ones as it's harder to remove an electron from a species which already has lack of negative charge.

The lowest electronic transition was calculated subtracting the energy of the LUMO (LUMO β for radical species) from the energy of the HOMO. Values obtained are shown in table 9. Wavelength of the transition was also calculated.

Table 9

Molecule		Orbitals involved in the transition	$\Delta E_{\text{LUMO-HOMO}}$ (eV)	λ (nm)	
Ethylene	Vacuum	Neutral	8-9	7,36	168
		Radical cation	8 α -8 β	3,49	356
Ethylene	Aqueous solution	Neutral	8-9	7,39	168
		Radical cation	8 α -8 β	3,46	358

TME	Vacuum	Neutral	24-25	5,91	210
		Radical cation	24 α -24 β	2,66	466
	Aqueous solution	Neutral	24-25	6,00	207
		Radical cation	24 α -24 β	2,69	461
TMOE	Vacuum	Neutral	40-41	5,69	218
		Radical cation	40 α -40 β	2,39	520
	Aqueous solution	Neutral	40-41	5,09	244
		Radical cation	40 α -40 β	2,40	516

In general it's observed a higher transition energy for neutral molecules than for radical cations, pointing out that the split in energy of a given orbital in two orbitals, α and β , is lower than the energy difference between two consecutive orbitals. Also, ΔE values is reduced as the number of atoms per molecule increases and the orbital numbers involved in the transition get higher too, indicating that as the orbital number increases the energy difference between two consecutive orbitals is smaller, statement that agrees with quantum mechanics basis.

Finally, in aqueous solution not a significant change was observed, in ethylene the same wavelength was obtained for the lowest electronic transition in vacuum and in aqueous media, in TME a slight difference is observed and in TMOE, although in the radical cation a similar wavelength was obtained, a higher difference is found in the neutral species. Probably this is because in vacuum some important delocalizations from donor NBO to acceptor NBO take place which lead to deviations from the Lewis structure, making the bonding in the molecule a bit different in the species in vacuum and in aqueous solution.

UV-Vis spectrum

UV-Visible spectra were obtained for ethylene, TME, TMOE and their corresponding radical cations in vacuum and in aqueous solution. For ethylene, the spectra for non-symmetrized neutral molecule and radical cation in vacuum were also obtained. In all cases the units of the absorptivity molar coefficient (epsilon) are $\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$.

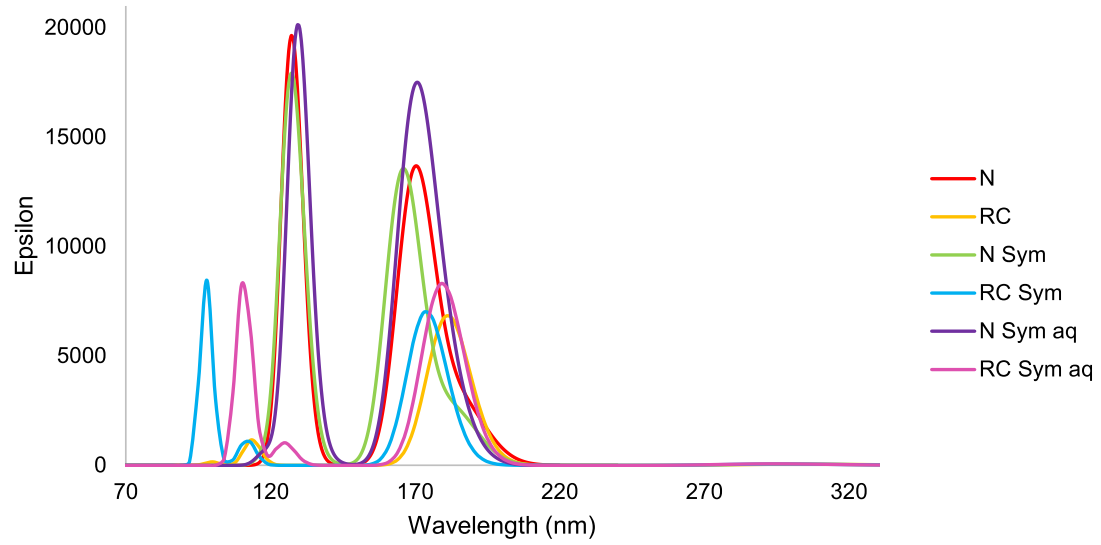


Figure 15. Ethylene UV-Vis spectrum

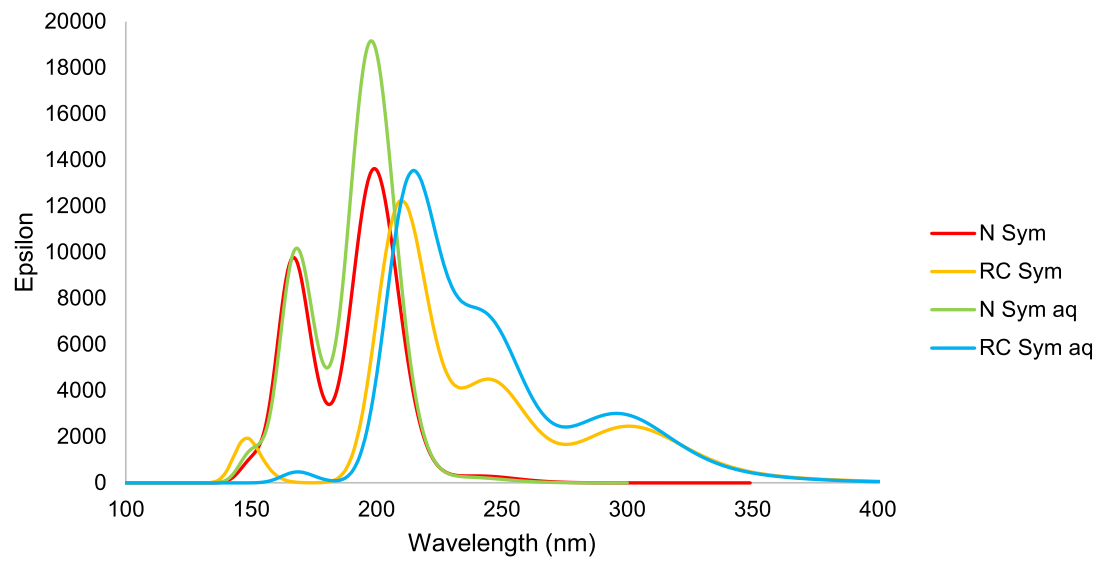


Figure 16. TME UV-Vis spectrum

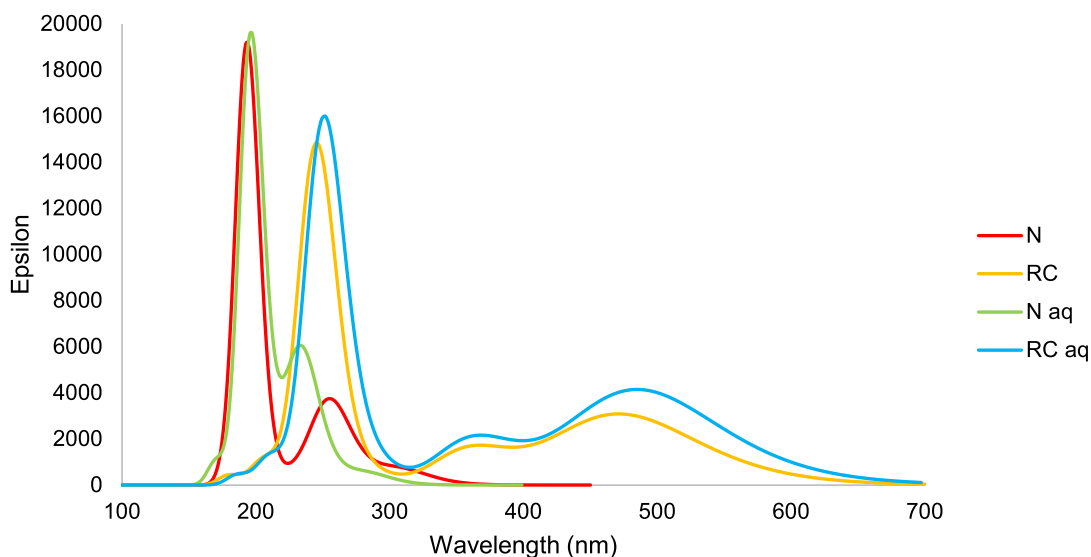


Figure 17. TMOE UV-Vis spectrum

In ethylene UV-Vis spectrum it is observed that in the neutral species very close values are obtained between symmetrized and non-symmetrized species, while in the radical cation more deviations take place, so more significant changes may happen in the radical cation when it changes from C_2 to C_{2h} symmetry than in the neutral molecule when changing from D_2 to D_{2h} symmetry.

In the three spectra there are significant differences between the neutral species and the radical cation, in TME and in TMOE absorption bands of the radical cation appear at higher wavenumbers than absorption bands of the neutral species, in ethylene that trend is not observed. In ethylene it can be appreciated how in aqueous solution a small shift towards higher wavenumbers takes place, but in TME and TMOE that tendency is not so clear. In general, slight changes are found in aqueous media.

When changing from ethylene to TME and then to TMOE it's observed that transitions at higher wavenumbers (lower energy) take place, because orbitals with a higher orbital number are occupied and energy difference is lower between them.

In neutral ethylene the lowest electronic transition, which was previously calculated, with a wavelength of 168 nm for vacuum and aqueous solution, is observed and the lowest electronic transition of the radical cation at 356 nm can be figured out, although it has a very small absorbance. In TME the lowest electronic transition for the neutral species, which is around 210 nm in vacuum and in aqueous solution, is found but for the radical

cation, which is around 460 nm, it's not observed. In TMOE the lowest electronic transition for the neutral molecule in vacuum, which is around 220 nm, is found and in aqueous solution, which is around 240, also, but for the radical cation which is around 520 nm for vacuum and aqueous media it's not so clear. In conclusion, lowest electronic transitions for neutral molecules can clearly be observed in the spectrum, but for radical cations to see them is harder.

Conclusions

Obtained results for the studied magnitudes (Gibbs free energy, reduction potential, symmetry, vibrations, molecular orbitals & NBO, ionization energies, lowest electronic transitions and UV-Vis spectrum for ethylene, tetramethylethylene, tetramethoxyethylene and their corresponding radical cations, in vacuum and in aqueous solution) led to the following conclusions:

1. Radical cations are significantly less stable than parent molecules.
2. Aqueous media stabilizes the radical cation and the double bond in ethylene and in tetramethylethylene but destabilizes tetramethoxyethylene.
3. Alkoxy substituents stabilize the double bond and the radical cation better than alkyl substituents through electron donation of the oxygen atom, whereas alkyl substituents stabilize double bonds and radical cations better than hydrogen.
4. When a molecule is converted into its radical cation the symmetry of the species gets reduced. The same happens when neutral tetramethylethylene changes from vacuum to aqueous solution.
5. Shape and symmetry of molecular orbitals changes significantly when changing from the neutral species to the radical cation.

Conclusiones

Los resultados obtenidos para las magnitudes estudiadas (energía libre de Gibbs, potencial de reducción, simetría, vibraciones, orbitales moleculares y NBO, energías de ionización, transiciones electrónicas más bajas y espectro UV-Vis para el etileno, tetrametiletileno, tetrametoxietileno y sus correspondientes radicales cationes, en vacío y en disolución acuosa) llevaron a las siguientes conclusiones:

1. Los radicales cationes son significativamente menos estables que las moléculas neutras.
2. El medio acuoso estabiliza el radical catión y el doble enlace en el etileno y en tetrametiletileno, pero desestabiliza el tetrametoxietileno.
3. Los sustituyentes alcoxi estabilizan el doble enlace y el radical catión mejor que los sustituyentes alquilo a través de la donación electrónica del átomo de oxígeno, mientras que los sustituyentes alquilo estabilizan los dobles enlaces y los radicales cationes mejor que el hidrógeno.
4. Cuando una molécula se convierte en su radical catión, la simetría de la especie se reduce. Lo mismo sucede cuando el tetrametiletileno neutro cambia de vacío a disolución acuosa.
5. La forma y la simetría de los orbitales moleculares cambian significativamente cuando se cambia de la especie neutra al radical catión.

Conclusións

Os resultados obtidos para as magnitudes estudadas (enerxía libre de Gibbs, potencial de redución, simetría, vibracións, orbitais moleculares e NBO, enerxías de ionización, transicións electrónicas máis baixas e espectro UV-Vis para o etileno, tetrametiletieno, tetrametoxietieno e os seus correspondentes radicais catións, en baleiro e en disolución acuosa) levaron ás seguintes conclusións:

6. Os radicais catións son significativamente menos estables que as moléculas neutras.
7. O medio acuoso estabiliza o radical catión e o dobre enlace no etileno e no tetrametiletieno, pero desestabilizan o tetrametoxietieno.
8. Os substituíntes alcoxi estabilizan o dobre enlace e o radical catión mellor que os substituíntes alquilo a través da doazón electrónica do átomo de osíxeno, mentres que os substituíntes alquilo estabilizan os dobres enlaces e os radicais catións mellor que o hidróxeno.
9. Cando unha molécula convértese no seu radical catión, a simetría da especie redúcese. O mesmo sucede cando o tetrametiletieno neutro cambia de baleiro a disolución acuosa.
10. A forma e a simetría dos orbitais moleculares cambian significativamente cando se cambia da especie neutra ao radical catión.

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Annex

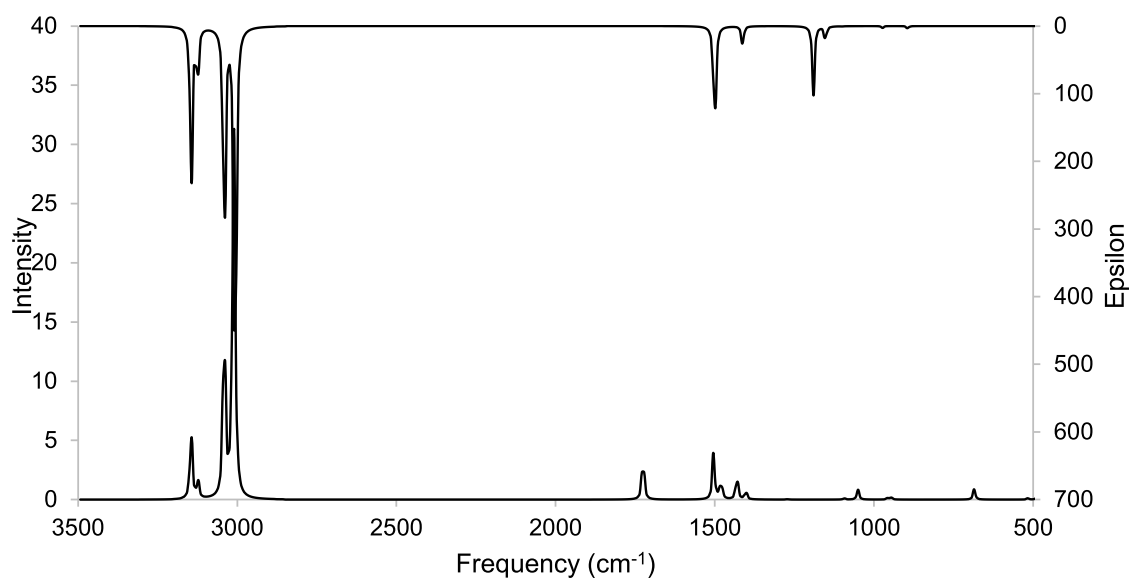


Figure 18. TME in vacuum

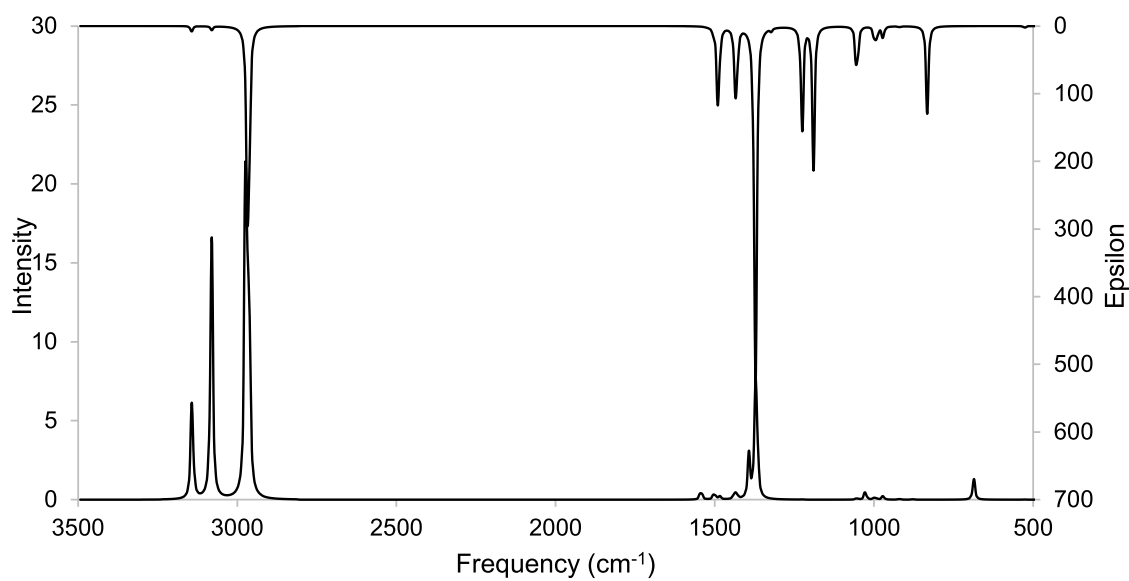


Figure 19. TME radical cation in vacuum

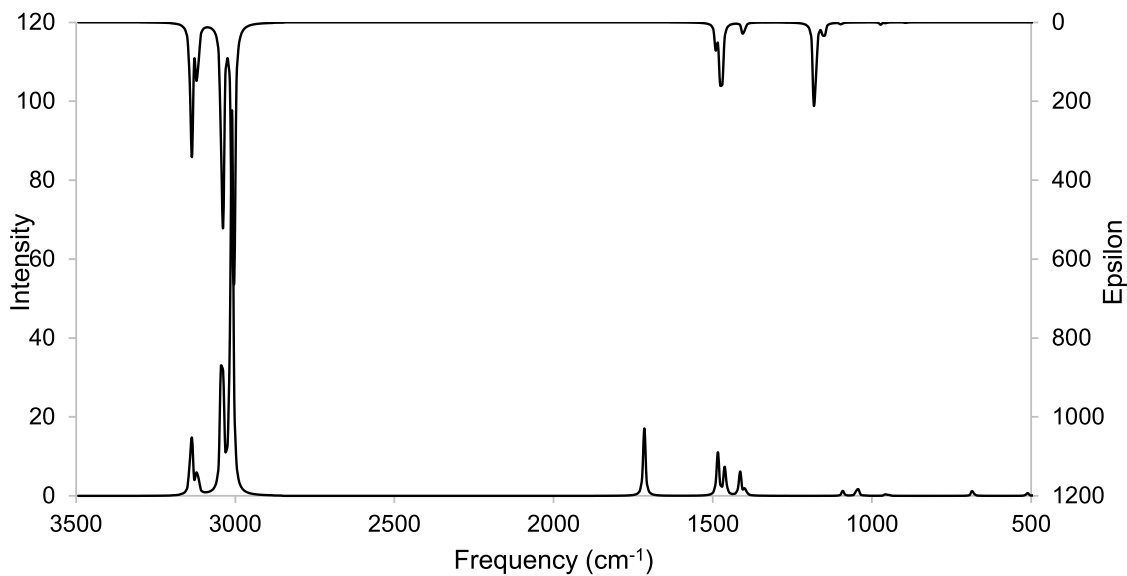


Figure 20. TME aqueous solution

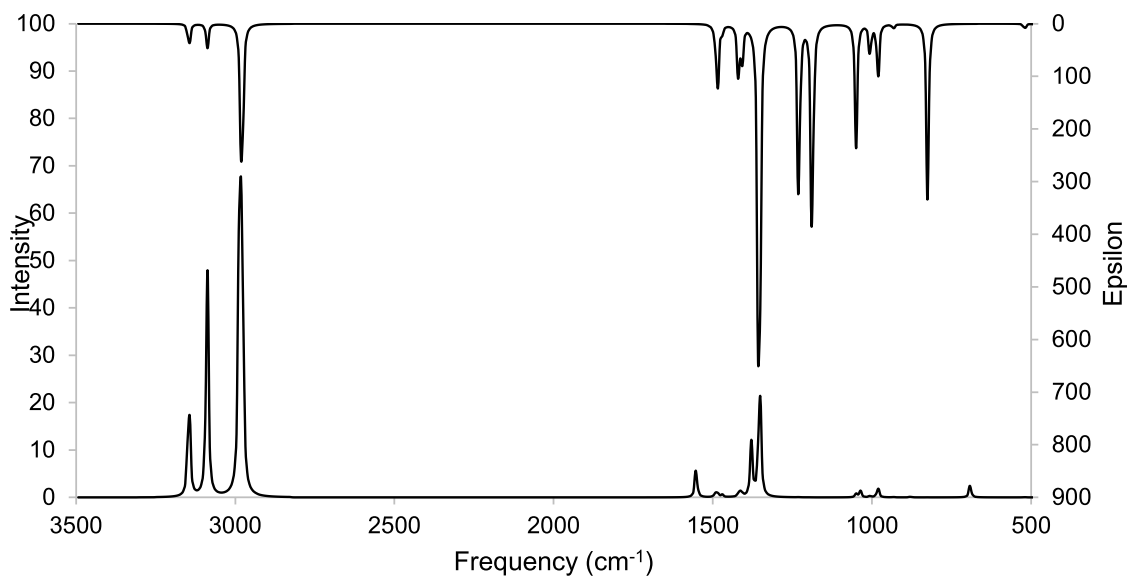


Figure 21. TME radical cation in aqueous solution

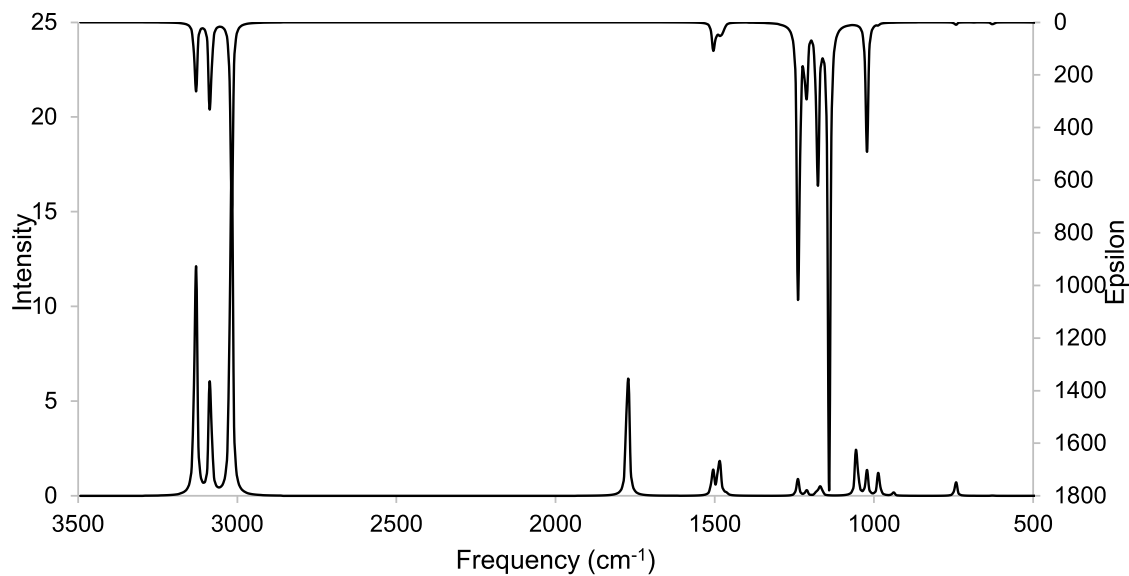


Figure 22. TMOE in vacuum

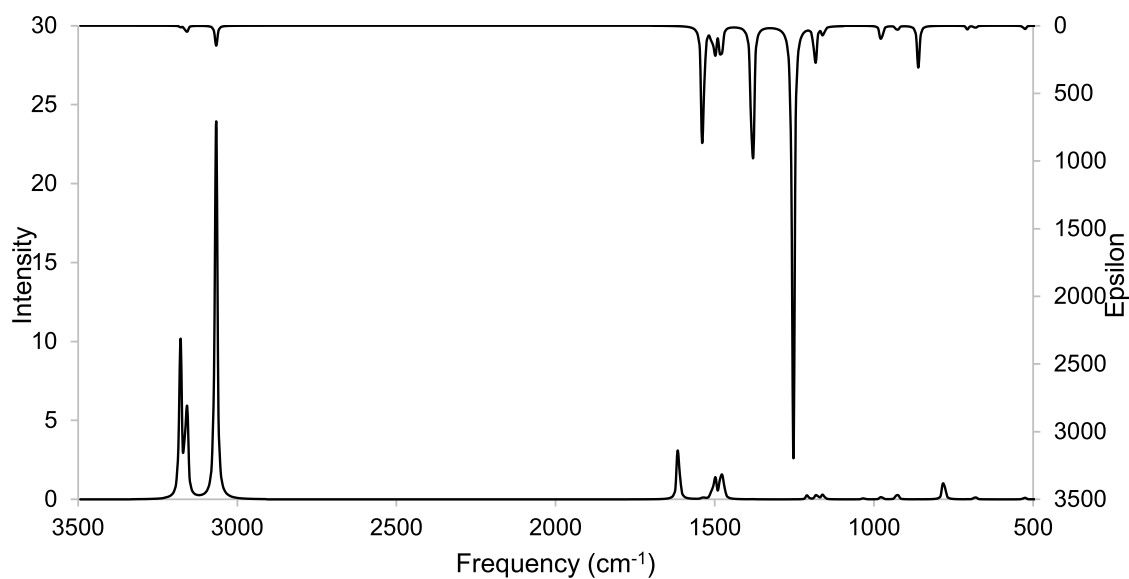


Figure 23. TMOE radical cation

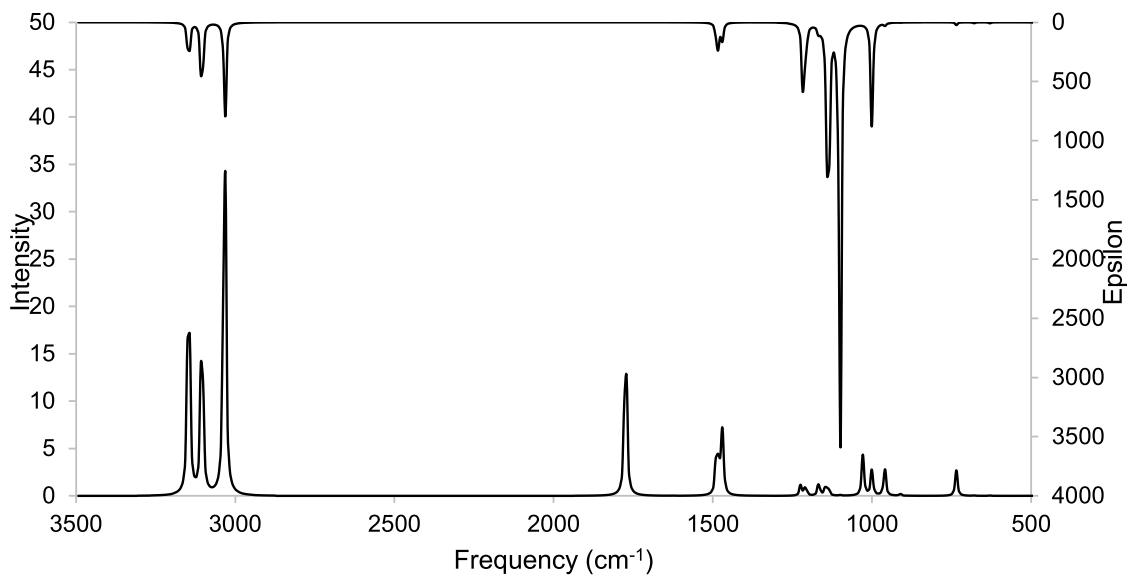


Figure 24. TMOE in aqueous solution

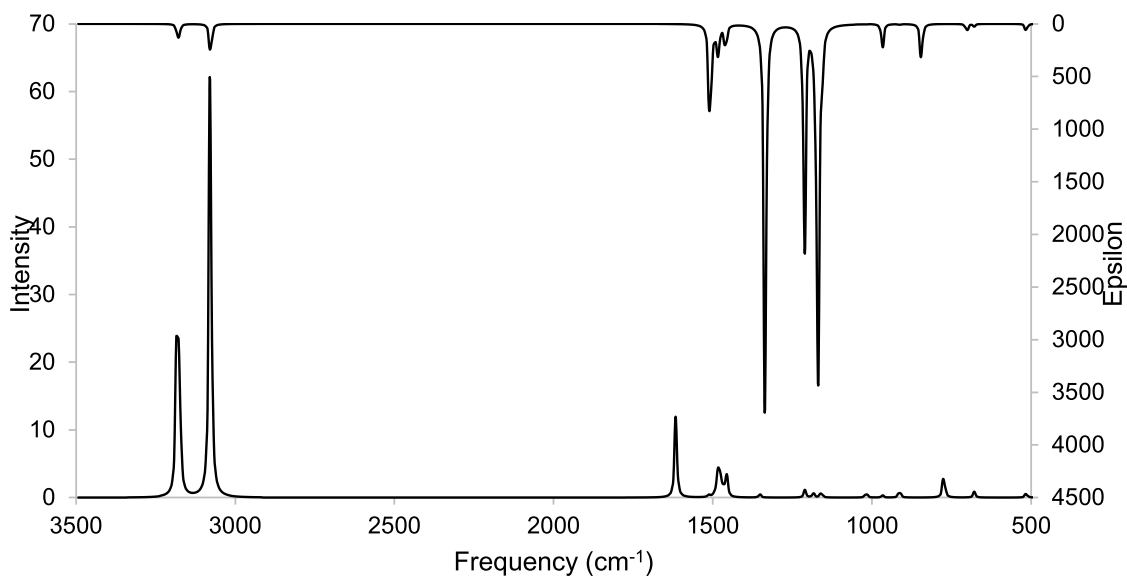


Figure 25. TMOE radical cation in aqueous solution

Table 10. Difference between vibration frequencies of vibrational modes in neutral molecules and in radical cations.

Vibration frequency (neutral molecule - radical cation); cm⁻¹

Vibration mode	Ethylene		TME		TMOE	
	Vacuum	Aqueous solution	Vacuum	Aqueous solution	Vacuum	Aqueous solution
1	231,74	204,59	-56,64	3,04	-1,72	1,57
2	184,23	188,19	-7,55	-6,00	-5,54	-0,81
3	86,84	112,17	7,83	9,91	-5,72	-23,39
4	-16,38	-8,94	-11,73	-2,92	-60,54	-60,41
5	36,49	28,58	-23,46	-2,26	-44,19	-47,22
6	105,84	83,35	36,32	16,80	-2,48	-18,18
7	45,09	52,18	19,05	14,46	-5,13	-28,95
8	182,53	180,7	23,71	3,03	-10,26	-34,38
9	39,83	10,13	-20,19	-20,61	-28,78	-48,3
10	51,63	18,26	14,26	7,57	15,82	33,06
11	14,56	-17,95	-10,24	-8,39	17,93	-8,23
12	23,45	-12,72	-1,2	-7,61	40	31,1
13			61,61	68,22	59,79	32,79
14			66,53	67,02	34,85	21,56
15			35,93	23,49	26,96	18,27
16			2,01	-8,16	36,96	34,18
17			27,46	14,24	100	114,14
18			51,87	39,41	5,28	1,19
19			66,12	54,69	36,64	32,52
20			47,23	47,18	-37,32	-38,91
21			-37,43	-36,75	78,67	66,03
22			-35,7	-49,79	58,35	46,7
23			-51,27	-54,94	45,66	33,21
24			34,61	46,05	21,74	10,5
25			37,9	45,73	-15,61	-55,9
26			41,2	49,48	3,82	-18,8
27			56,86	58,69	5,23	-11,57
28			79,29	82,16	4,56	3,42
29			46,3	54,01	-11,31	-4,5

30	45,49	48,43	-4,03	-17,38
31	53,36	53,27	-4,2	-16,31
32	11,86	1,88	2,09	-3,9
33	10,55	-10,84	-40,45	-1,95
34	-0,54	-2,94	-144,81	-120,15
35	2,21	-3,86	-141,83	-128,45
36	181,89	162,70	-10,57	7,98
37	40,23	27,46	-12,97	5,83
38	39,89	27,09	-5,68	10,96
39	38,63	24,15	-1,76	11,06
40	38,74	25,91	5,46	-2,88
41	-41,77	-47,47	5,58	-3,06
42	-41,64	-47,13	-12,73	-9,52
43	-39,76	-47,81	-12,41	-7,46
44	-40,95	-47,14	-6,88	-7,32
45	-16,13	-23,70	-6,62	-8,2
46	-15,22	-24,40	-28,39	-21,72
47	1,58	-8,42	-30,99	-25,18
48	0,82	-8,16	158,92	157,58
49			-45,96	-43,67
50			-45,54	-43,22
51			-48,4	-45,8
52			-47,86	-45,11
53			-74,29	-70,08
54			-73,98	-70,05
55			-75,45	-72,02
56			-75,42	-71,98
57			-46,46	-35,65
58			-46,48	-35,66
59			-48,08	-37,23
60			-47,71	-37,17

Table 11. Difference between vibration frequencies of vibrational modes in vacuum and in aqueous solution.

Vibration frequency (vacuum - aqueous solution); cm⁻¹

Vibration mode	Ethylene		TME		TMOE	
	Neutra l	Radical cation	Neutra l	Radical cation	Neutra l	Radical cation
1	2,27	-24,88	-68,12	-8,44	8,18	11,47
2	-3,82	0,14	-11,74	-10,19	4,48	9,21
3	-13,3	12,03	0,85	2,93	5	-12,67
4	-4,58	2,86	-4,65	4,16	9,98	10,11
5	8,25	0,34	-11,33	9,87	1,8	-1,23
6	17,75	-4,74	5,42	-14,1	14,39	-1,31
7	10,42	17,51	5,89	1,3	11,43	-12,39
8	10,98	9,15	6,72	-13,96	-0,17	-24,29
9	3,74	-25,96	1,28	0,86	-0,09	-19,61
10	4,07	-29,3	1,28	-5,41	-22,84	-5,6
11	1,46	-31,05	4,42	6,27	3,36	-22,8
12	3,9	-32,27	1,08	-5,33	-13,04	-21,94
13			0,62	7,23	4,94	-22,06
14			-1,48	-0,99	1,75	-11,54
15			-0,41	-12,85	4,75	-3,94
16			0,26	-9,91	4,34	1,56
17			-1,27	-14,49	-2,87	11,27
18			4,68	-7,78	7,37	3,28
19			1,98	-9,45	8,25	4,13
20			4,04	3,99	8	6,41
21			1,4	2,08	28,16	15,52
22			10,02	-4,07	25,4	13,75
23			1,18	-2,49	22,37	9,92
24			5,38	16,82	26,23	14,99
25			11,25	19,08	41,06	0,77
26			9,58	17,86	23,52	0,9
27			15,98	17,81	18,57	1,77
28			10,99	13,86	2,05	0,91
29			13,6	21,31	2,32	9,13

30	18,51	21,45	10,04	-3,31
31	20	19,91	12,71	0,6
32	22,65	12,67	4,7	-1,29
33	25,42	4,03	3,37	41,87
34	16,65	14,25	21,37	46,03
35	14,13	8,06	16,15	29,53
36	10,06	-9,13	-2,96	15,59
37	-1,06	-13,83	-1,6	17,2
38	-0,98	-13,78	3,16	19,8
39	0,9	-13,58	7,15	19,97
40	0,13	-12,7	15,02	6,68
41	-1,93	-7,63	14,48	5,84
42	-1,44	-6,93	13,69	16,9
43	0,25	-7,8	11,87	16,82
44	-0,45	-6,64	16,65	16,21
45	4,5	-3,07	16,63	15,05
46	5,53	-3,65	19,54	26,21
47	6,83	-3,17	19,14	24,95
48	6,62	-2,36	-0,26	-1,6
49			-14,36	-12,07
50			-14,42	-12,1
51			-13,93	-11,33
52			-14,39	-11,64
53			-20,73	-16,52
54			-20,45	-16,52
55			-19,78	-16,35
56			-19,74	-16,3
57			-15,49	-4,68
58			-15,49	-4,67
59			-15,78	-4,93
60			-15,47	-4,93