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Vertical and Adiabatic Ionization Potentials of Fluorinated, Chlorinated, and Chlorofluorinated Ethylenes Using G2 and G3 Theories

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Adiabatic ionization potentials (AIPs) and vertical ionization potentials (VIPs) for all fluorinated, chlorinated, and chlorofluorinated ethylenes have been determined by ab initio computations. The calculated AIPs give a mean absolute deviation of 0.014 eV at G2 and 0.015 eV at G3 theories compared to experimental values. We have estimated AIPs (in eV) for AIP ((*E*)-CHCl═CFCl) = 9.59, AIP ((*Z*)-CHCl═CFCl) = 9.60, AIP (CCl_2═CFCl) = 9.42, and AIP (CHF═CCl_2) = 9.65. Furthermore, our calculated AIPs values of 9.58 eV for (*Z*)-CFCl═CFCl and 9.56 eV for (*E*)-CFCl═CFCl are very different from the experimental data of 10.2 eV. VIPs are calculated by Koopmans's theorem with HF methodology and by G2 and G3 theories. Koopmans's theorem fails in giving a good description of the behavior of the VIPs for fluoroethylenes. Furthermore, significant improvement in the results is observed by the mean absolute deviation from experimental data on the computed values (0.242 eV using the 6-311+G(3df,2p) basis set and 0.248 eV using the GTlarge basis set, compared with 0.049 eV at G2 and 0.045 eV at G3 theories) when orbital relaxation and changes in electronic correlation and zero-point energies are taken into account. Our estimated VIPs values calculated by G3 theory (in eV) are VIP ((*E*)-CHCl═CFCl) = 9.89, VIP ((*Z*)-CHCl═CFCl) = 9.90, VIP ((*E*)-CFCl═CHF)= 10.26, VIP ((*Z*)-CFCl═CHF) = 10.25, VIP ((*E*)-CFCl═CFCl) = 9.93, VIP ((*Z*)-CFCl═CFCl) = 9.96, VIP (CCl_2═CFCl) = 9.71, VIP (CF_2═CHCl) = 10.19, VIP (CHF═CCl_2) = 9.96, VIP (CH_2═CFCl) = 10.32, VIP ((*Z*)-CHCl═CHF) = 10.16, and VIP ((*E*)-CHCl═CHF) = 10.16. Furthermore, the variation of the VIPs and AIPs with the increase in the number of halogen atoms in the molecules presents different patterns to chloroethylenes and fluoroethylenes.

Introduction

Chlorinated, fluorinated, and chlorofluorinated ethylenes are substances with large use in polymers, as polyvinylchloride and polytetrafluoroethylene and recently in the development of 1,2-dichloro-1,2-difluoroethylene in electrophotographic photoreceptors,[1,2] and in displays.[3] Also, the understanding of the thermochemical properties of these species leads to an important role in environmental and atmospheric chemistry reactions. We are interested in the estimation of thermochemical properties, such as ionization potentials, for chlorinated, fluorinated, and chlorofluorinated ethylenes because there are a lack of experimental values for some of them and few results for others. Furthermore, it is known that the Gaussian-*n* series, Gaussian 1,[4] Gaussian 2,[5] and Gaussian 3,[6] have been developed to achieve a target accuracy of ±2 kcal mol^{-1} or ± 0.1 eV with respect to experimental data. Generally, it would also take accurate predictions where the experimental data are unknown or uncertain. Moreover, the ionization can be examined as a vertical or adiabatic ionization process.

The aim of this work is to investigate vertical ionization potentials, VIPs, and adiabatic ionization potentials, AIPs, of all chlorinated, fluorinated, and chlorofluorinated ethylenes using G2 and G3 theories.

Calculation of the vertical ionization potential has been investigated by Koopmans's theorem,[7−11] which states that the ionization potential is equal to the negative of the orbital energy of the detached electron. The effects of orbital relaxation and changes in the correlation energy and zero-point energy corrections at the vertical ionization potentials have been also investigated; these aspects are neglected by Koopmans's theorem but are important to achieve results in better agreement with experimental ones.[10,11] In the vertical ionization process, the geometry of the molecule undergoing ionization keeps the geometry of the neutral one.[8,12]

Instead of this, in the adiabatic ionization process, beyond the changes in energy by the processes indicated above, the geometry of the molecule can change,[8,12] and the energy necessary to detach an electron is reduced. The AIP process can be treated as a two-step process, first the VIP process and, after that, the second step, with relaxation of the molecular structure and, for both, changes in the correlation and the zero-point energies, besides the orbital relaxation.

The difference between the energy parameters of the ionization process for fluoroethylenes, chloroethylenes, and chlorofluoroethylenes is also investigated with the aim to understand how AIPs and VIPs change with the substitution of hydrogen atoms by halogen atoms in the ethylene frame.

Moreover, our results are compared with previously calculated VIPs and AIPs.

Theoretical Framework and Computational Procedure

All calculations have been carried out using the Gaussian 98[13] and Gaussian 03[14] package of programs. The procedures

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to investigate vertical ionization potentials and adiabatic ionization potentials are described as follows.

Vertical Ionization Potential (VIP). The vertical ionization potential is the minimal energy needed for the detachment of an electron, but different from the adiabatic process, there is not time for the molecule to undergo geometry changes (for example, when a technique such as fast electron bombardment is used); therefore, the geometry of the ionized molecule is the same as that of the neutral one.[8]

Two approaches have been used, one considering the Koopmans's theorem, which states that the ionization potential required to remove an electron from an orbital is given by the negative value of the energy of this orbital, $-\epsilon$, as calculated within the Hartree–Fock approximation[7,8] for the neutral molecule. The other approach consists of the difference between the values of energy of the ionized molecule, with the same geometry as that of the neutral one, and the energy of the neutral molecule, and in this case, different from Koopmans's theorem, it is assumed that the orbitals can relax and that the correlation energy can change in the ionized molecule.

First, the energies and geometries of neutral molecules were obtained by G2 and G3 theoretical calculations. The orbitals and Hartree–Fock single-point energies were obtained with the Hartree–Fock (HF) level using GTlarge and 6-311+G(3df,2p) basis sets on the equilibrium geometry that resulted from MP2-(full)/6-31G(d) (into the final step of G3 and G2 theories). Second, the energies of the ionized molecules were obtained with G2 and G3 theories keeping the geometries obtained previously with MP2(full)/6-31G(d) from the neutral molecules frozen. The Hartree–Fock single-point energies of the ionized molecules were obtained using GTlarge and 6-311+G(3df,2p) basis sets on the geometry of the neutral molecule obtained with MP2(full)/6-31G(d). To verify how the changes in correlation energy, the zero-point energy, and the energy relaxation of the orbitals affect the vertical ionization energy, we used the same analysis as that of Maksić and Vianello.[12]

For positive as well as for neutral molecules, the zero-point energy was calculated from harmonic frequencies acquired with HF/6-31G(d) and scaled by a factor of 0.8929. All calculations were done with spin-restricted calculations for the neutrals molecules and spin-unrestricted calculations for the ionized molecules.

By Koopmans's theorem, the vertical ionization potential (VIP) was obtained by

$$\mathrm{VIP} = E(\mathrm{HF})_{n-1}^{\mathrm{Koop}} - E(\mathrm{HF})_n = -\epsilon \tag{1}$$

where the index n is the number of electrons in the neutral molecule and $n - 1$ denotes the cation. $E(\mathrm{HF})_{n-1}^{\mathrm{Koop}}$ is the energy calculated with the clamped nuclei and considering the orbitals frozen when one electron is removed, and $E(\mathrm{HF})_n$ is the energy obtained at the neutral molecule. The difference between both energies is equal the negative energy of the HOMO orbital, $-\epsilon$. This value assumes that there is neither relaxation in the orbitals nor changes in correlation energy and zero-point energy.

On the basis of orbital relaxation, but keeping the nuclei clamped, the vertical ionization potential obtained with Hartree–Fock model, VIP(HF), results from

$$\mathrm{VIP(HF)} = E(\mathrm{HF})_{n-1}^{\mathrm{CN}} - E(\mathrm{HF})_n + \Delta\mathrm{ZPE}_{n,n-1}^{\mathrm{CN}} \tag{2}$$

where

$$\Delta\mathrm{ZPE}_{n,n-1}^{\mathrm{CN}} = \mathrm{ZPE}_{n-1}^{\mathrm{CN}} - \mathrm{ZPE}_n \tag{3}$$

and $\mathrm{ZPE}_{n-1}^{\mathrm{CN}}$ is the zero-point energy of the ionized molecule with the clamped nuclei (as indicated by superscript CN), while ZPE_n the zero-point energy of the neutral molecule.

Including changes in the correlation energy, we have VIP-(GX), with X as 2 or 3 relating to G2 and G3 theories, respectively

$$\mathrm{VIP}(\mathrm{G}X) = E(\mathrm{G}X)_{n-1}^{\mathrm{CN}} - E(\mathrm{G}X)_n \tag{4}$$

where $E(\mathrm{G}X)_{n-1}^{\mathrm{CN}}$ is the energy obtained with GX theory at the ionized molecule with the clamped nuclei, and $E(\mathrm{G}X)_n$ is the energy obtained with the GX theory at the neutral molecule.

Since the correlation energy is taken as a positive value for convenience, each term in eq 4 can be

$$E(\mathrm{G}X)_{n-1}^{\mathrm{CN}} = E(\mathrm{HF})_{n-1}^{\mathrm{CN}} - E(\mathrm{corr})_{n-1}^{\mathrm{CN}} + \mathrm{ZPE}_{n-1}^{\mathrm{CN}} \tag{5}$$

$$E(\mathrm{G}X)_n = E(\mathrm{HF})_n - E(\mathrm{corr})_n + \mathrm{ZPE}_n \tag{6}$$

where $E(\mathrm{corr})_{n-1}^{\mathrm{CN}}$ is the correlation energy of the ionized molecule with the same geometry as that of the neutral one, and $E(\mathrm{corr})_n$ is the correlation energy of the neutral molecule.

Substituting eqs 5 and 6 into 4 and using eq 2 results in

$$\mathrm{VIP}(\mathrm{G}X) = \mathrm{VIP(HF)} + \Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} \tag{7}$$

where

$$\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} = E(\mathrm{corr})_n - E(\mathrm{corr})_{n-1}^{\mathrm{CN}} \tag{8}$$

VIP(HF) can be entered into eq 7 because, in G2 and G3 theories, ZPEs are calculated at the same Hartree–Fock level of theory.

VIP(HF) can also be expressed by the orbital energy, $-\epsilon$, the orbital relaxation energy keeping the nuclei fixed, $E\mathrm{r}_{n-1}^{\mathrm{CN}}$, and the $\Delta\mathrm{ZPE}_{n,n-1}^{\mathrm{CN}}$ energies

$$\mathrm{VIP(HF)} = -\epsilon + E\mathrm{r}_{n-1}^{\mathrm{CN}} + \Delta\mathrm{ZPE}_{n,n-1}^{\mathrm{CN}} \tag{9}$$

where

$$E\mathrm{r}_{n-1}^{\mathrm{CN}} = E(\mathrm{HF})_{n-1}^{\mathrm{CN}} - E(\mathrm{HF})_n + \epsilon \tag{10}$$

Thus, adding eq 9 into eq 7, the final equation is given as

$$\mathrm{VIP}(\mathrm{G}X) = -\epsilon + E\mathrm{r}_{n-1}^{\mathrm{CN}} + \Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} + \Delta\mathrm{ZPE}_{n,n-1}^{\mathrm{CN}} \tag{11}$$

Adiabatic Ionization Potential (AIP). The adiabatic ionization potential is the minimal energy needed for the detachment of an electron when the ion is produced in its most stable state; this means that the molecular geometry changes (which is the case in, e.g., photoionization or photoelectron spectroscopic techniques).[8]

The adiabatic ionization potential, AIP(GX), was obtained by the difference between the energy (electronic and zero-point correction) of the ionized molecule and the energy of the neutral molecule, both obtained by G2 and G3 theories; therefore

$$\mathrm{AIP}(\mathrm{G}X) = E(\mathrm{G}X)_{n-1} - E(\mathrm{G}X)_n \tag{12}$$

where $E(\mathrm{G}X)_{n-1}$ is the radical cation energy with the relaxed structure.

Using the analysis of Maksić and Vianello,[12] we may treat the adiabatic ionization potential as a two-step process. The first step corresponds to the vertical ionization, and the second corresponds to the relaxed structural parameters of the radical cation. Establishing $E\mathrm{r(nucl)}_{n-1}$ as the relaxation energy of the relaxed orbitals without constrains in the geometry structure and $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ as the change in the correlation energy due the optimization of radical cation geometry, one obtains

$$E\mathrm{r(nucl)}_{n-1} = E(\mathrm{HF})_{n-1} - E(\mathrm{HF})^{\mathrm{CN}}_{n-1} \tag{13}$$

and

$$\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1} = E(\mathrm{corr})^{\mathrm{CN}}_{n-1} - E(\mathrm{corr})_{n-1} \tag{14}$$

where $E(\mathrm{HF})_{n-1}$ is the Hartree−Fock energy, and $E(\mathrm{corr})_{n-1}$ is the correlation energy of the radical cation with a relaxed structure. The superscript RN denotes relaxed nuclei.

Therefore, AIP may be defined as

$$\mathrm{AIP}(\mathrm{G}X) = \mathrm{VIP}(\mathrm{G}X) + E\mathrm{r(nucl)}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1} + \Delta \mathrm{ZPE}^{\mathrm{RN}}_{n-1,n-1} \tag{15}$$

and

$$\Delta \mathrm{ZPE}^{\mathrm{RN}}_{n-1,n-1} = \mathrm{ZPE}_{n-1} - \mathrm{ZPE}^{\mathrm{CN}}_{n-1} \tag{16}$$

where ZPE_{n-1} is the ZPE energy of the radical cation with a relaxed structure.

Results

For all molecules studied, the detached electron was localized in the HOMO orbital, that is, the π orbital between the carbon atoms. All optimized geometries, for both neutral and positively charged haloethylenes, were planar, and no imaginary frequencies were achieved. The G2 and G3 theories give a planar structure for the ethylene cation, but the experimentally derived geometry by Köppel et al.[15] shows a twisted structure with dihedral angles of 25°. Therefore, we have calculated the relaxed structure of the cation utilizing this structure, keeping it frozen. Abrams et al.[16] already showed the deficiencies in several methods and basis sets to obtain the cation structure, and these deficiencies explain why the G2 and G3 theories were not able to give the correct geometry. All of the geometries of the halogenated ethylenes were tested using UB3LYP/6-311+G(d,p) because this method results in the twisted structure of the ethylene with a low computational cost. Nevertheless, all of the calculated halogenated ethylene structures result in planar geometries, even when starting the optimization jobs from twisted geometries with dihedral angles of 25° and tightening the cutoffs on forces and the step sizes used to determine the convergence to the final structure.

Tables 1 and 2 show the vertical and adiabatic ionization potentials obtained in this work using G2 and G3 theories, respectively, and the selected experimental ionization potentials. Table 3 shows the VIP(HF) both from G2 and G3 calculations. For further analysis, the haloethylenes were organized in three groups, fluoroethylenes (group F), chloroethylenes (group Cl), and chlorofluoroethylenes (group FCl), in increasing number of halogen atoms.

The experimental values presented in Tables 1, 2, and 3 were selected from the literature (see Table S4 in Supporting Information), and the closest values to the calculated ones were chosen. G2/G3, ZPE, and Hartree−Fock energies are given in the Supporting Information (Tables S1, S2, and S3, respectively).

Figures 1−3, 5−7, 9, 10, 12, and 13 show $-\epsilon$, $E\mathrm{r}^{\mathrm{CN}}_{n-1}$, $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$, VIP(HF), VIP(G$X$), $E\mathrm{r(nucl)}_{n-1}$, $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$, $\Delta \mathrm{ZPE}^{\mathrm{RN}}_{n-1,n-1}$, and AIP(G3) as a function of the number of halogen atoms, respectively. Figure 8 shows the relations between VIP(G3) and $-\epsilon$, and Figures 4 and 11 show $E\mathrm{r}^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ and $E\mathrm{r(nucl)}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ as a function of the number of halogen atoms, respectively. All of the figures show G3 theory results, while G2 theory results have the same behavior and are displayed in the Supporting Information (Figures S1−S13).

AIPs for 1,2-dichloro-1,2-difluoroethylene isomers differ by about 0.62 eV from the experimental data. However, it is suggested by Lias et al.[17] that the experimental value are not trustworthy; therefore, ours calculations confirm this statement. In view of this, average absolute deviations of the calculated AIPs from the experimental data were obtained without considering the deviations on 1,2-dichloro-1,2-difluoroethylene isomers. Results of AIP(G3) and VIP(G3) from G2 and G3 theoretical calculations have about the same average absolute deviation from the experimental data. While G3 results have average absolute deviations of 0.015 and 0.045 eV for the AIP and VIP experimental data, respectively, G2 results have average absolute deviations of 0.014 and 0.049 eV. The HOMO energy according to Koopmans's theorem gives average absolute deviations, compared with the same experimental data, of 0.248 and 0.242 eV, while VIP(HF) has average absolute deviations of 1.08 and 1.09 eV for GTlarge and 6-311+G(3df,2p) basis set calculations, respectively.

The present results allow one to recognize the different behavior of the parameters used in the calculations of VIP and AIP as a function of the number of halogen atoms for fluoroethylenes, chloroethylenes, and chlorofluoroethylenes. Of particular significance is the variation of $E\mathrm{r}^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ as a function of the number of halogen atoms. These quantities do not cancel each other and are important to achieve the closest results to experimental data, while Koopmans's theorem gives comparatively poor results. Good linear and polynomial fits, with correlation coefficients larger than 0.9, can be achieved for VIP versus $-\epsilon$ only for chloroethylenes; however, as can be seen in Figure 8, it is possible to observe that VIP increases rapidly with $-\epsilon$, while for the fluoroethylenes, the results are relatively constant. We will now analyze these different behaviors of fluoroethylenes and chloroethylenes and compare our results with previous calculations.

Discussion

One first aspect to be concerned with is the difference in the geometry of the ethylene cation and the haloethylenes. Both G2 and G3 theories were not able to give the correct structure for the ethylene cation as determined experimentally, and this fact can be explained by deficiencies in the method and basis set[16] of the optimization step in the G2 and G3 calculations. With the UB3LYP/6-311+G(d,p) calculation, the twisted structure of ethylene is reached, but for the haloethylenes, the resulting structures are planar. One possible explanation for this fact is the presence of p orbitals with lone pairs in the F and Cl atoms in the same plane as the p orbitals of the π bond between the carbons. The interaction between these p orbitals results in the planar structure for the ground state of the haloethylene cations. Besides, it is known that inductive and mesomeric effects of F and Cl atoms occur in organic compounds; thus, the mesomeric +M effect could release electrons to the carbon atoms after the ionization process, favoring the planar structures

TABLE 1: Vertical (VIPs) and Adiabatic (AIPs) Ionization Potentials Obtained by G2 Theory, in eV, and Deviations from Experimental Data

substance	$-\epsilon^a$	Er^{CN}_{n-1}	$\Delta E(\text{corr})^{CN}_{n,n-1}$	$\Delta ZPE^{CN}_{n,n-1}$	VIP(G2)^a	VIP exp.	$Er(\text{nucl})_{n-1}$	$\Delta E(\text{corr})^{RN}_{n-1,n-1}$	$\Delta ZPE^{RN}_{n-1,n-1}$	AIP(G2)^a	AIP exp.
$CH_2=CH_2$	10.26 (−0.42)	−1.35	1.88	−0.037	10.75 (0.07)	10.68^b	−0.04	−0.10	−0.057	10.55 (0.04)	10.51 ± 0.01^b
group Cl											
$CHCl=CH_2$	10.11 (−0.04)	−1.20	1.30	−0.029	10.18 (0.03)	10.15^b	−0.25	0.09	−0.025	9.99 (0.00)	9.99 ± 0.02^b
(*E*)-$CHCl=CHCl$	9.94 (0.14)	−1.10	1.00	−0.018	9.82 (0.02)	9.80^b	−0.29	0.08	−0.012	9.6 (0.0)	9.6^c
(*Z*)-$CHCl=CHCl$	9.98 (0.18)	−1.13	1.03	−0.029	9.85 (0.05)	9.80^b	−0.27	0.06	−0.014	9.63 (−0.02)	9.65 ± 0.01^c
$CCl_2=CH_2$	10.14 (0.14)	−1.26	1.18	−0.032	10.03 (0.03)	10.00^b	−0.30	0.10	−0.029	9.80 (0.01)	9.79 ± 0.04^d
$CCl_2=CHCl$	9.9 (0.3)	−1.16	0.92	−0.021	9.7 (0.1)	9.6^e	−0.29	0.07	−0.011	9.45 (−0.00)	9.45 ± 0.01^c
$CCl_2=CCl_2$	9.9 (0.4)	−1.17	0.83	−0.012	9.5 (0.0)	9.5^e	−0.28	0.05	−0.004	9.30 (−0.02)	9.32 ± 0.01^c
group F											
$CHF=CH_2$	10.51 (−0.12)	−1.31	1.53	−0.034	10.70 (0.07)	10.63 ± 0.02^b	−0.40	0.09	−0.022	10.37 (0.00)	10.37 ± 0.02^c
(*E*)-$CHF=CHF$	10.68 (0.05)	−1.27	1.26	−0.027	10.64 (0.01)	10.63 ± 0.02^b	−0.65	0.19	−0.005	10.18 (±0.03)	10.21 ± 0.02^b 10.15 ± 0.02^b
(*Z*)-$CHF=CHF$	10.71 (0.09)	−1.26	1.25	−0.037	10.66 (0.04)	10.62 ± 0.02^b	−0.63	0.19	−0.006	10.21 (0.01^f)	10.23 ± 0.02^b 10.20 ± 0.02^b
$CF_2=CH_2$	10.77 (0.07)	−1.32	1.33	−0.042	10.74 (0.04)	10.70 ± 0.02^b	−0.64	0.22	−0.020	10.30 (0.00)	10.30^c
$CF_2=CHF$	10.92 (0.30)	−1.27	1.06	−0.033	10.68 (0.06)	10.62 ± 0.02^b	−0.84	0.29	0.000	10.13 (−0.01)	10.14 ± 0.02^b
$CF_2=CF_2$	11.14 (0.45)	−1.25	0.87	−0.028	10.73 (0.04)	10.69 ± 0.02^b	−1.01	0.37	0.014	10.10 (0.00 or -0.01)	10.10^b 10.11^c
group FCl											
(*E*)-$CHCl=CHF$	10.25	−1.17	1.09	−0.022	10.15		−0.44	0.15	−0.008	9.85 (−0.02)	9.87 ± 0.01^c
(*Z*)-$CHCl=CHF$	10.26	−1.16	1.09	−0.032	10.16		−0.42	0.14	−0.010	9.87 (0.00)	9.87 ± 0.01^c
$CFCl=CH_2$	10.40	−1.28	1.24	−0.037	10.32		−0.44	0.15	−0.024	10.01 (0.04)	9.97^b
(*E*)-$CFCl=CHF$	10.51	−1.23	1.01	−0.028	10.26		−0.60	0.21	−0.005	9.86 (0.03)	9.83 ± 0.02^c
(*Z*)-$CFCl=CHF$	10.49	−1.22	1.01	−0.030	10.25		−0.61	0.22	−0.006	9.85 (−0.01)	9.86 ± 0.02^c
$CHCl=CF_2$	10.43	−1.15	0.94	−0.031	10.19		−0.59	0.21	−0.004	9.81 (−0.03)	9.84^c
(*E*)-$CFCl=CHCl$	10.12	−1.12	0.92	−0.025	9.89		−0.42	0.14	−0.008	9.60	
(*Z*)-$CFCl=CHCl$	10.16	−1.17	0.94	−0.026	9.90		−0.43	0.14	−0.009	9.60	
$CCl_2=CHF$	10.20	−1.20	0.97	−0.024	9.95		−0.42	0.13	−0.008	9.65	
$CFCl=CF_2$	10.66 (0.40)	−1.20	0.84	−0.024	10.28 (0.02)	10.26^b	−0.75	0.27	0.009	9.81 (−0.01)	9.82^b
(*E*)-$CFCl=CFCl$	10.31	−1.19	0.83	−0.022	9.93		−0.55	0.19	0.003	9.57 (−0.63)	10.2 ± 0.1^{d,g}
(*Z*)-$CFCl=CFCl$	10.33	−1.20	0.85	−0.021	9.96		−0.56	0.19	0.004	9.59 (−0.61)	10.2 ± 0.1^{d,g}
$CCl_2=CF_2$	10.35 (0.53)	−1.18	0.82	−0.021	9.97 (0.15)	9.82 ± 0.02^b	−0.56	0.20	0.003	9.61 (−0.01)	9.62^b
$CCl_2=CFCl$	10.08	−1.18	0.83	−0.017	9.71		−0.40	0.11	−0.001	9.42	

[a] Deviations (values in parentheses) are the difference between the calculated value and the experimental one without considering the uncertainties. [b] Ref 18. [c] Ref 20. [d] Ref 17. [e] Ref 19. [f] Deviation from the experimental value of 10.20 eV. [g] There is no indication of *Z* or *E* isomers for that value, referent to 598-88-9 CAS registry number substance.

of the haloethylenes. Furthermore, the release of an electron from the p orbital of fluoro atoms to the p orbitals of the carbon atom, as the release of electrons from carbon to the fluoro atom in the σ bond, was yet observed in calculations for neutral tetrafluoroethylene.[21] More calculations, for example, to determine bond orders and charges, are necessary to confirm this hypothesis.

Because of little experimental data available to allow us to made an accurate analysis for the chlorofluoroethylenes, we decided to focus on a discussion for the different behavior of fluorinated and chlorinated compounds in VIP and AIP calculations. However, we can delineate from the Figures 1−13 that the chlorofluoroethylenes have, in general, a behavior that is a mixture of the behaviors of the fluoroethylenes and the

TABLE 2: Vertical (VIPs) and Adiabatic (AIPs) Ionization Potentials Obtained by G3 Theory, in eV, and Deviations from Experimental Data

substance	$-\epsilon$[a]	Er^{CN}_{n-1}	$\Delta E(\text{corr})^{CN}_{n,n-1}$	ΔZPE	VIP(G3)[a]	VIP exp.	$Er(\text{nucl})_{n-1}$	$\Delta E(\text{corr})^{RN}_{n-1,n-1}$	$\Delta ZPE^{RN}_{n-1,n-1}$	AIP(G3)[a]	AIP exp.
$CH_2=CH_2$	10.26 (−0.42)	−1.35	1.85	−0.037	10.72 (0.04)	10.68[b]	−0.04	−0.09	−0.057	10.53 (0.02)	10.51 ± 0.01[b]
group Cl											
$CHCl=CH_2$	10.11 (−0.04)	−1.21	1.31	−0.029	10.18 (0.03)	10.15[b]	−0.24	0.08	−0.025	9.99 (0.00)	9.99 ± 0.02[b]
(*E*)-$CHCl=CHCl$	9.96 (0.16)	−1.13	1.02	−0.018	9.83 (0.03)	9.80[b]	−0.29	0.06	−0.012	9.6 (0.0)	9.6[c]
(*Z*)-$CHCl=CHCl$	9.97 (0.17)	−1.13	1.03	−0.029	9.84 (0.04)	9.80[b]	−0.28	0.07	−0.014	9.62 (−0.03)	9.65 ± 0.01[c]
$CCl_2=CH_2$	10.13 (0.13)	−1.25	1.18	−0.032	10.03 (0.03)	10.00[b]	−0.29	0.09	−0.029	9.80 (0.01)	9.79 ± 0.04[d]
$CCl_2=CHCl$	9.9 (0.3)	−1.16	0.93	−0.021	9.7 (0.1)	9.6[e]	−0.28	0.05	−0.011	9.44 (−0.01)	9.45 ± 0.01[c]
$CCl_2=CCl_2$	9.9 (0.4)	−1.18	0.84	−0.012	9.5 (0.0)	9.5[e]	−0.28	0.04	−0.004	9.29 (−0.03)	9.32 ± 0.01[c]
group F											
$CHF=CH_2$	10.52 (−0.11)	−1.32	1.52	−0.034	10.69 (0.06)	10.63 ± 0.02[b]	−0.39	0.09	−0.022	10.37 (0.00)	10.37 ± 0.02[c]
(*E*)-$CHF=CHF$	10.70 (0.07)	−1.27	1.24	−0.027	10.64 (0.01)	10.63 ± 0.02[b]	−0.63	0.18	−0.005	10.18 (±0.03)	10.21 ± 0.02[b] 10.15 ± 0.02[b]
(*Z*)-$CHF=CHF$	10.72 (0.10)	−1.26	1.23	−0.037	10.65 (0.03)	10.62 ± 0.02[b]	−0.62	0.20	−0.006	10.22 (−0.01[f])	10.23 ± 0.02[b] 10.20 ± 0.02[b]
$CF_2=CH_2$	10.78 (0.08)	−1.31	1.30	−0.042	10.73 (0.03)	10.70 ± 0.02[b]	−0.63	0.22	−0.020	10.30 (0.00)	10.30[c]
$CF_2=CHF$	10.94 (0.32)	−1.26	1.03	−0.033	10.68 (0.06)	10.62 ± 0.02[b]	−0.83	0.28	0.000	10.13 (−0.01)	10.14 ± 0.02[b]
$CF_2=CF_2$	11.16 (0.47)	−1.24	0.84	−0.028	10.73 (0.04)	10.69 ± 0.02[b]	−1.00	0.37	0.014	10.11 (0.00 or −0.01)	10.10[b] 10.11[c]
group FCl											
(*E*)-$CHCl=HF$	10.25	−1.17	1.10	−0.022	10.16		−0.43	0.13	−0.008	9.85 (−0.02)	9.87 ± 0.01[c]
(*Z*)-$CHCl=CHF$	10.26	−1.16	1.09	−0.032	10.16		−0.42	0.14	−0.010	9.87 (0.00)	9.87 ± 0.01[c]
$CFCl=CH_2$	10.41	−1.28	1.23	−0.037	10.32		−0.44	0.15	−0.024	10.01 (0.04)	9.97[b]
(*E*)-$CFCl=CHF$	10.52	−1.23	1.00	−0.028	10.26		−0.60	0.21	−0.005	9.86 (0.03)	9.83 ± 0.02[c]
(*Z*)-$CFCl=CHF$	10.50	−1.22	1.00	−0.030	10.25		−0.60	0.20	−0.006	9.84 (−0.02)	9.86 ± 0.02[c]
$CHCl=CF_2$	10.41	−1.12	0.93	−0.031	10.19		−0.58	0.20	−0.004	9.81 (−0.03)	9.84[c]
(*E*)-$CFCl=CHCl$	10.15	−1.16	0.92	−0.025	9.89		−0.41	0.12	−0.008	9.59	
(*Z*)-$CFCl=CHCl$	10.16	−1.17	0.94	−0.026	9.90		−0.43	0.14	−0.009	9.60	
$CCl_2=CHF$	10.21	−1.21	0.98	−0.024	9.96		−0.42	0.12	−0.008	9.65	
$CFCl=CF_2$	10.68 (0.42)	−1.20	0.82	−0.024	10.28 (0.02)	10.26[b]	−0.75	0.27	0.009	9.81 (−0.01)	9.82[b]
(*E*)-$CFCl=CFCl$	10.31	−1.18	0.82	−0.022	9.93		−0.54	0.17	0.003	9.56 (−0.64)	10.2 ± 0.1[d,g]
(*Z*)-$CFCl=CFCl$	10.34	−1.20	0.84	−0.020	9.96		−0.55	0.17	0.004	9.58 (−0.62)	10.2 ± 0.1[d,g]
$CCl_2=CF_2$	10.35 (0.53)	−1.18	0.82	−0.021	9.97 (0.15)	9.82 ± 0.02[b]	−0.54	0.18	0.003	9.61 (−0.01)	9.62[b]
$CCl_2=CFCl$	10.07	−1.17	0.83	−0.017	9.71		−0.40	0.11	−0.001	9.42	

[a] Deviations (values in parentheses) are the difference between the calculated value and the experimental one without considering the uncertainties. [b] Ref 18. [c] Ref 20. [d] Ref 17. [e] Ref 19. [f] Deviation from the experimental value of 10.23 eV. [g] There is no indication of *Z* or *E* isomers for that value, referent to 598-88-9 CAS registry number substance.

chloroethylenes; moreover, their values are between those of the chloroethylenes and the fluoroethylenes too.

Vertical Ionization Potentials (VIP). Most of the values of $-\epsilon$, which represent the VIP by Koopmans's theorem, have positive deviations from experimental results, with the exception of ethylene, chloroethylene, and fluoroethylene. In the VIP calculation outlined by Koopmans's theorem, changes in energy caused by orbital relaxation, changes in vibrational frequencies, and changes in electronic correlation energy are not considered, while VIP(HF) values, which consider changes in energy caused by orbital relaxation and changes in frequencies but do not consider changes in correlation energy (taken as a positive quantity), are significantly low when compared with the experimental VIP values.

TABLE 3: Vertical Ionization Potentials from Hartree−Fock Calculations, VIP(HF), Obtained by G2 and G3 Theories, in eV, and Deviations from Experimental Data

substance	VIP(HF)[a] 6-311+G(3df,2p)	VIP(HF)[a] GTlarge	VIP exp.
$CH_2{=}CH_2$	8.87	8.87	10.68[b]
	(−1.81)	(−1.81)	
group Cl			
$CHCl{=}CH_2$	8.88	8.87	10.15[b]
	(−1.27)	(−1.28)	
(*E*)-CHCl=CHCl	8.82	8.81	9.80[b]
	(−0.98)	(−0.99)	
(*Z*)-CHCl=CHCl	8.82	8.81	9.80[b]
	(−0.98)	(−0.99)	
$CCl_2{=}CH_2$	8.85	8.85	10.00[b]
	(−1.15)	(−1.15)	
$CCl_2{=}CHCl$	8.8	8.8	9.6[b]
	(−0.8)	(−0.8)	
$CCl_2{=}CCl_2$	8.7	8.7	9.5[b]
	(−0.8)	(−0.8)	
group F			
$CHF{=}CH_2$	9.17	9.17	10.63
	(−1.46)	(−1.46)	± 0.02[b]
(*E*)-CHF=CHF	9.38	9.40	10.63
	(−1.25)	(−1.23)	± 0.02[b]
(*Z*)-CHF=CHF	9.41	9.42	10.62
	(−1.21)	(−1.20)	± 0.02[b]
$CF_2{=}CH_2$	9.41	9.43	10.70
	(−1.29)	(−1.27)	± 0.02[b]
$CF_2{=}CHF$	9.62	9.65	10.62
	(−1.00)	(−0.97)	± 0.02[b]
$CF_2{=}CF_2$	9.86	9.89	10.69
	(−0.83)	(−0.80)	± 0.02[b]
group FCl			
(*E*)-CHCl=CHF	9.06	9.06	
(*Z*)-CHCl=CHF	9.07	9.07	
$CFCl{=}CH_2$	9.08	9.09	
(*E*)-CFCl=CHF	9.25	9.26	
(*Z*)-CFCl=CHF	9.24	9.25	
$CHCl{=}CF_2$	9.25	9.26	
(*E*)-CFCl=CHCl	8.98	8.97	
(*Z*)-CFCl=CHCl	8.96	8.96	
$CCl_2{=}CHF$	8.98	8.98	
$CFCl{=}CF_2$	9.44	9.46	10.26[b]
	(−0.82)	(−0.80)	
(*E*)-CFCl=CFCl	9.10	9.11	
(*Z*)-CFCl=CFCl	9.11	9.12	
$CCl_2{=}CF_2$	9.15	9.15	9.82
	(−0.67)	(−0.67)	± 0.02[b]
$CCl_2{=}CFCl$	8.88	8.88	

[a] Deviations (values in parentheses) are the difference between the calculated value and the experimental one without considering the uncertainties. [b] Ref 18.

The VIP(G*X*) procedure gives positive deviations compared with the experimental results, meaning that the calculated values are a little high. However, the VIP(G*X*) values are very close to the experimental data. Among the values of $-\epsilon$ and VIP(HF) and VIP(G*X*), the last have better agreement with the experimental data because the average absolute deviations of VIP(G2) and VIP(G3) compared to the experimental values are 0.049 and 0.045 eV, respectively, while the average absolute deviation of VIP(HF) related to the same experimental values, using the 6-311+G(3df,2p) basis set, is 1.09 eV, and using the GTlarge basis set, the average absolute deviation is 1.08 eV. Also, the average absolute deviation of $-\epsilon$, using the 6-311+G(3df,2p) basis set, is 0.242 eV, and using the GTlarge basis set, the deviation is 0.248 eV.

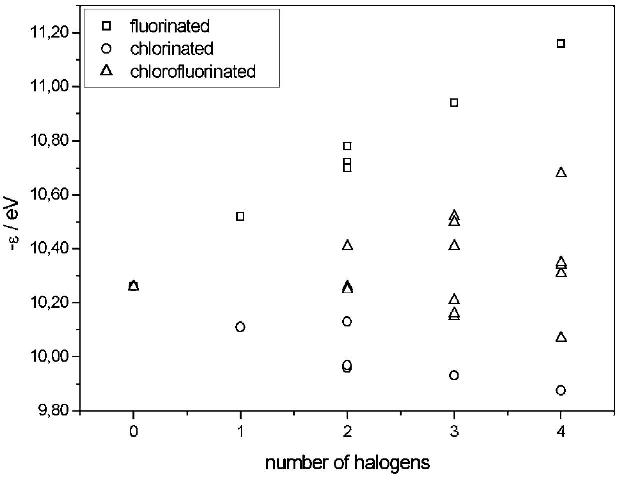

Figure 1. HOMO energy as a function of the number of halogens (G3 theory results).

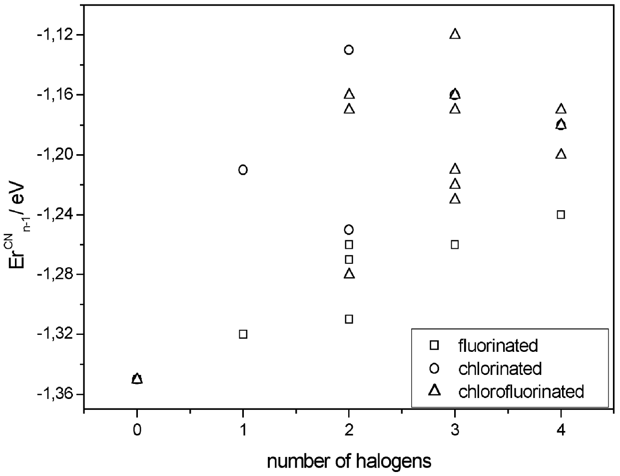

Figure 2. Er^{CN}_{n-1} as a function of the number of halogens (G3 theory results).

Figure 1 shows the different behavior of the HOMO energy, $-\epsilon$, as a function of the number of halogen atoms for the haloethylenes. While $-\epsilon$ increases with the addition of fluoro atoms in the fluoroethylenes, it decreases in the chloroethylenes when chloro atoms are added to the molecule. One possible way to explain this is by the inductive and mesomeric effects. In the fluorinated molecules, the inductive +I effect predominates over the mesomeric +M effect, and the carbon atoms become more positively charged with the addition of fluoro atoms, resulting in a hindrance to withdraw the electron in the ionization process, raising the HOMO energy. Yet, for the chloroethylenes, the mesomeric effect predominates over the inductive effect, and the chloro atoms release electrons to the carbon atoms that becomes less positively charged, making the withdrawal of the electron in the ionization process easier, and therefore, the HOMO energy decreases with the increase of chloro atoms in the molecule.

Figure 2 shows Er^{CN}_{n-1} as a function of the number of halogen atoms in the molecule. Only the fluoroethylenes behave well, with Er^{CN}_{n-1} rising smoothly, and the other substances have VIP(G*X*) values above those of fluoroethylenes. For the chloroethylenes, the Er^{CN}_{n-1} rises more than that for the fluoroethylenes adding chloro atoms to the molecule but shows a poor behavior. The difference in the Er^{CN}_{n-1} values for the (*E*)- and (*Z*)-CHCl=CHCl isomers, whose values are −1.13 eV, in comparison with the $CCl_2{=}CH_2$ isomer, whose value is −1.25 eV, displays a height dependence of the relaxation energy with the disposition of the chloro atoms in the molecule.

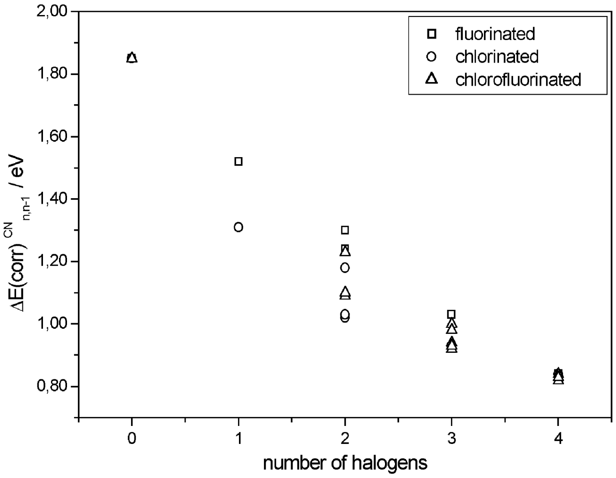

Figure 3. $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ as a function of the number of halogens (G3 theory results).

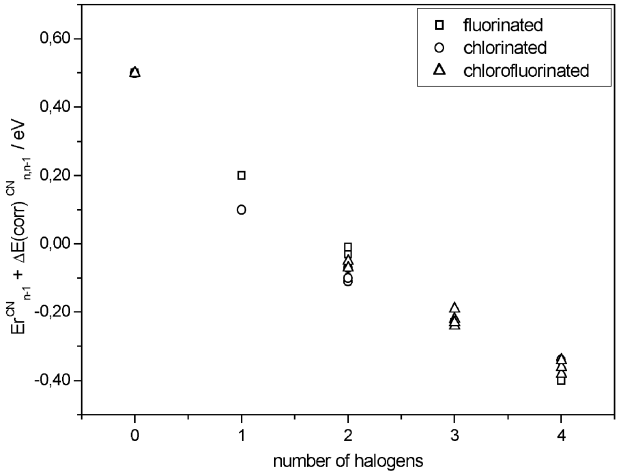

Figure 4. $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ as a function of the number of halogens (G3 theory results).

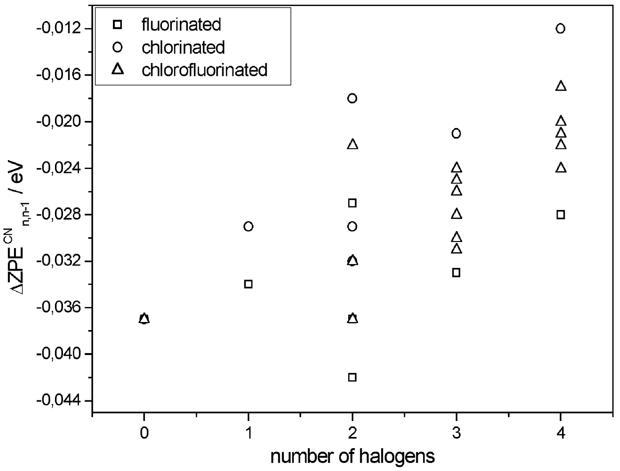

Figure 5. $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$ as a function of the number of halogens (G3 theory results).

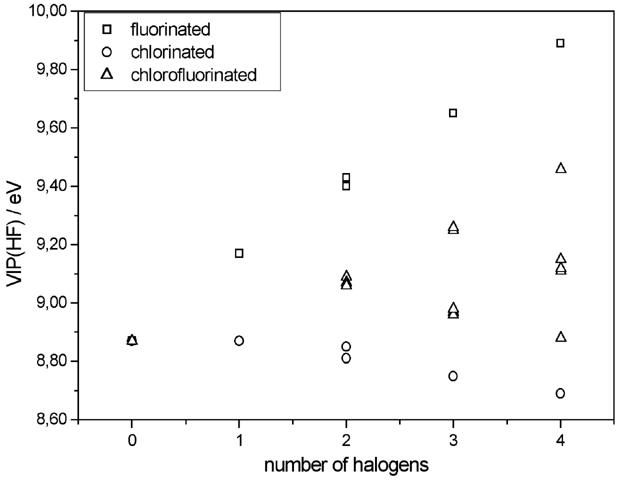

Figure 6. VIP(HF) as a function of the number of halogens (G3 theory results).

Figure 3 shows how the correlation energy changes with the addition of halogens to the molecule. The general trend observed is that the values decrease with the number of halogen atoms. The $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values for the fluoroethylenes have a smooth decreasing behavior, while for the chloroethylenes, the values rapidly decrease at the beginning and slowly at the ending. The decreasing of the $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ is expected because, as the number of electrons in the molecule increases, the correlation energy of the molecule becomes less sensitive to a withdrawal of one electron.

The $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values predominate over the Er^{CN}_{n-1} values for substances such as chloroethylene, fluoroethylene, and 1,1-difluoroethylene, and that makes VIP(GX) higher than $-\epsilon$, except for the calculated VIP(GX) of 1,1-difluoroethylene, whose values of $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ and Er^{CN}_{n-1} are nearly the same, in modulo, and in such cases, $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$ decreases the VIP(GX) value. For all others species, Er^{CN}_{n-1} predominates over $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, and this make VIP(G$X$) lower than $-\epsilon$.

As shown in Figure 4, the values of $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ are close to zero for substances with two fluoro atoms, and the Er^{CN}_{n-1} and $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values nearly cancel each other. For these compounds, $-\epsilon$ and VIP(GX) have closer values. The values of $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ decrease (Figure 3) with the addition of halogen atoms in the molecule; however. the Er^{CN}_{n-1} values increase (Figure 2). But, the range of the increase in Er^{CN}_{n-1} is small (about 0.23 eV), while $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ decreases significantly (about 1.03 eV). This explains why the $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values (Figure 4) diminish with the number of halogen atoms in the molecule.

Figure 5 shows the variation of the zero-point energy as a function of the number of halogens in haloethylenes. For all of the substances, the $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$ values rise with an increasing number of halogen atoms in the molecule. For the chloroethylenes, the increasing is more pronounced than that for the fluoroethylenes. The range of values varies by 0.03 eV; therefore, the contribution of the $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$ values to final VIP values is small, and the major contribution to the VIPs are given by the Er^{CN}_{n-1} and $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values.

Figure 6 shows the VIP(HF) as a function of the number of halogens in the molecule. As VIP(HF) takes into account only the variation of the relaxation and zero-point energies and as the relaxation energy predominates over $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$, it is expected that VIP(HF) behaves as an addition of the HOMO energy and Er^{CN}_{n-1}, and thus, it occurs that the behavior of VIP(HF) is the same as that of HOMO but with lower values (Er^{CN}_{n-1} has a negative value and decreases the positive value of the HOMO energy).

In Figure 7, VIP(G3) as a function of the number of halogen atoms in the molecule is shown. As in the HOMO behavior, the fluoroethylenes have higher values than the chloroethylenes.

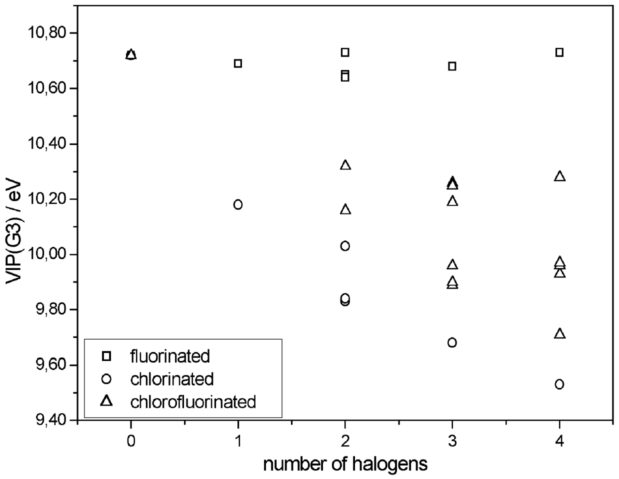

Figure 7. VIP(G3) as a function of the number of halogens (G3 theory results).

However, while the HOMO energies for the fluoroethylenes increase with the number of halogen atoms, the VIP(G3) values are nearly constant. This occurs because $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ has the exact contrary behavior of the HOMO energy, decreasing with the number of fluoro atoms. Both effects annul each other, and the result is a nearly constant value of VIP(G3) for the fluoroethylenes. For the chloroethylenes, the HOMO energy decreases with the number of chloro atoms, and the $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values have the same behavior; therefore, the effects are added, and the VIP(G3) values for these compounds decrease more sharply than the HOMO values.

An important point in Koopmans's theorem is to observe if $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ cancels with Er^{CN}_{n-1}. When this occurs, the theorem gives good previsions of the VIP values. However, as the behavior of $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ predominates over that of Er^{CN}_{n-1}, $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ behaves as $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, and the correlation energy has a predominant effect over the final values of the VIP(G*X*)s. Therefore, Koopmans's theorem fails to describe the behavior of the fluoroethylenes, as the HOMO energy increases with the number of fluoro atoms, while the VIP(G3) values decrease, initially, reaching a minimum for the difluoroethylenes and increasing after that. However, for the chloroethylenes, as the HOMO energies and the VIP(G*X*) values decrease with the number of chloro atoms, the behavior of the HOMO energy matches that of VIP(G*X*).

Quantitatively, Koopmans's theorem gives the closest results compared with the experimental data (deviations less than 0.10 eV) for difluoroethylene isomers when $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ nearly cancels with Er^{CN}_{n-1}. However, for the chlorinated ethylenes, Koopmans's theorem gives a closer result compared to the experimental VIP value only for the chloroethylene, not because $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ cancels with Er^{CN}_{n-1} but because the $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ value predominates.

As can be seen in Figure 8, it is possible to achieve correlation between VIP(G3) and Koopmans's VIPs for the chloroethylenes using a least-square fit and a third-order polynomial fit. The correlation factor to the least-square fit is 0.96463, and to the polynomial fit, it is 0.9755; the standard deviation to the least-square fit is 0.11335 and to the polynomial fit is 0.08688, and the equations are displayed as $\mathrm{VIP(G3)}_{\mathrm{lsCl}}$ and $\mathrm{VIP(G3)}_{\mathrm{poCl}}$.

The least-square fit is

$$\mathrm{VIP(G3)}_{\mathrm{lsCl}} = (-18.00 \pm 3.42) + (2.79 \pm 0.34)\mathrm{HOMO} \qquad (17)$$

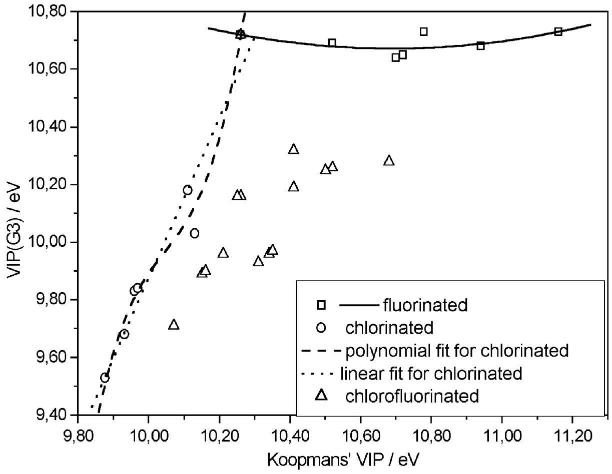

Figure 8. VIP(G3) as a function of the HOMO energy (G3 theory results). The polynomial fit to the fluoroethylenes is second order; the polynomial fit to the chloroethylenes is third order.

The third-order polynomial fit is

$$\mathrm{VIP(G3)}_{\mathrm{poCl}} = (-41246.29 \pm 22221.74) + (12319.01 \pm 6619.36)\mathrm{HOMO} + (-1226.30 \pm 657.20)\mathrm{HOMO}^2 + (40.70 \pm 21.75)\mathrm{HOMO}^3 \qquad (18)$$

Unfortunately, it was not possible to achieve a fit with a good correlation coefficient for the fluoroethylenes. The best fit was achieved with a second-order polynomial fit with a correlation coefficient of 0.41833 and standard deviation of 0.03471. The equation is displayed as $\mathrm{VIP(G3)}_{\mathrm{F}}$

$$\mathrm{VIP(G3)}_{\mathrm{F}} = (40.38 \pm 17.70) + (-5.56 \pm 3.31)\mathrm{HOMO} + (0.26 \pm 0.15)\mathrm{HOMO}^2 \qquad (19)$$

In the same way, VIP(HF) does not match the behavior of VIP(G*X*) for the fluoroethylenes because there is a lack of the $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ values.

The molecular structure given by the distribution of fluorine and chlorine atoms on the molecule makes the VIP(G*X*) values in the $CH_2{=}CY_2$ isomers bigger than those in the $CHY{=}CHY$ isomers (Y as Cl or F). That occurs because, in the HOMO energy, the $CH_2{=}CY_2$ isomers have larger values than in the $CHY{=}CHY$ isomers.

Because of the large deviation for the 1,1-dichloro-2,2-difluoroethylene value, we suggest other experimental measurements for this substance to confirm the experimental value, the single in literature.

Adiabatic Ionization Potentials (AIPs). In testing the applicability of the Gaussian-*n* series, it was observed that the average absolute deviations from the experimental values on adiabatic ionization potential calculations are 0.0611 eV for G2 theory and 0.0490 eV for G3 theory, supported by previous results with the G2/97 test set,[6] and recently, this test set was complemented by forming the G3/99[22] and G3/05[23] test sets, whose average absolute deviations are 0.0494 and 0.0477 eV, respectively. Our calculated adiabatic ionization potentials gives a mean absolute deviation of 0.014 eV at G2 and 0.015 eV at G3 theories compared to the experimental values, without considering the deviations from experimental data for the 1,2-dichloro-1,2-difluoroethylene isomers, because Lias et al.[17] suggest that the experimental value is not trustworthy. Also,

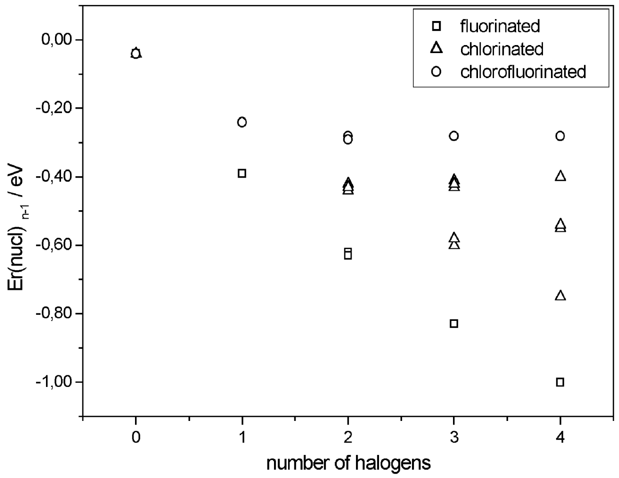

Figure 9. $E\mathrm{r}(\mathrm{nucl})_{n-1}$ as a function of the number of halogens (G3 theory results).

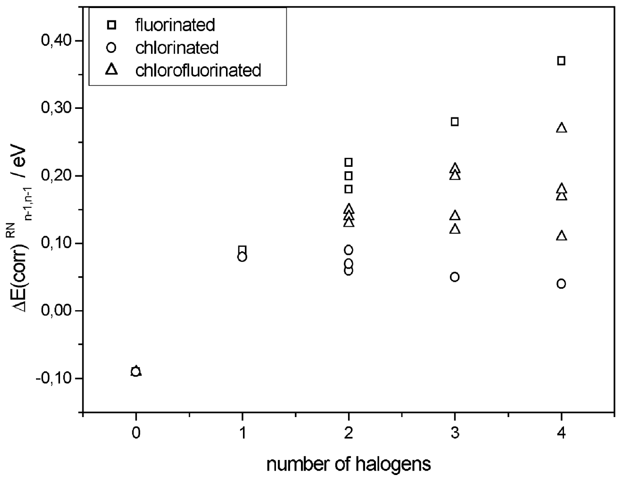

Figure 10. $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$as a function of the number of halogens (G3 theory results).

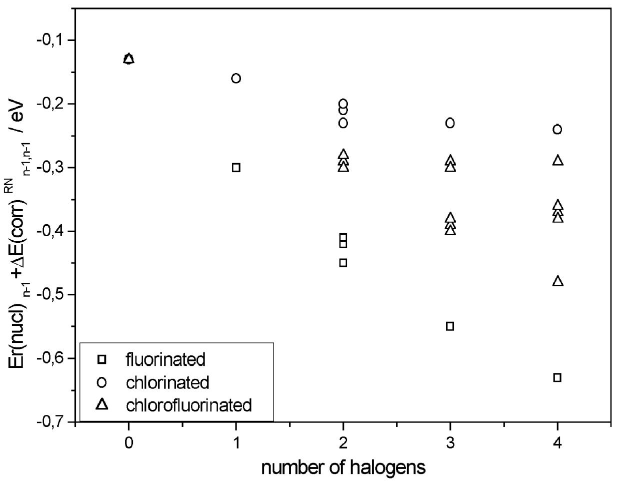

Figure 11. $E_{\mathrm{r}}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ as a function of the number of halogens (G3 theory results).

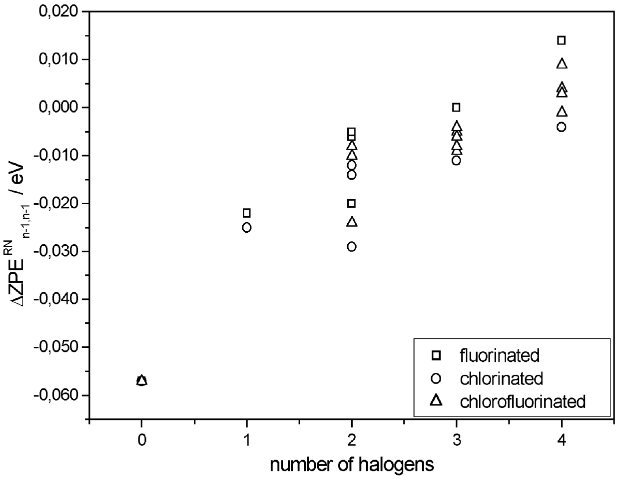

Figure 12. $\Delta \mathrm{ZPE}^{\mathrm{RN}}_{n-1,n-1}$ as a function of the number of halogens (G3 theory results).

only for these isomers are the deviations bigger than the average absolute deviations for the G2/97, G3/99, and G3/05 test sets.

The $E\mathrm{r}(\mathrm{nucl})_{n-1}$ as a function of the number of halogen atoms in the molecule is shown in the Figure 9. Again, the behavior of the fluorinated compounds is different than that of the chlorinated compounds. While $E\mathrm{r}(\mathrm{nucl})_{n-1}$ for the fluoroethylenes decrease steadily, for the chloroethylenes, it is nearly constant at about -0.26 eV. The effect of adding fluoro atoms in the fluoroethylenes is nearly additive, decreasing $E\mathrm{r}(\mathrm{nucl})_{n-1}$ by about 0.20 eV for each atom added.

Figure 10 shows the variation of $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ with the number of halogen atoms in the haloethylenes. Different from $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ for the fluoroethylenes increases with the number of fluoro atoms, while for the chloroethylenes, the values decrease a little (they decreased in $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$ too).

Figure 11 shows $E\mathrm{r}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ as a function of halogens for the haloethylenes. As the chloroethylenes have little variation in the $E\mathrm{r}(\mathrm{nucl})_{n-1}$ and $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ values, the sum of these parameters has little variation too, decreasing with the increase in the number of chloro atoms, following the behavior of $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$. However, $E\mathrm{r}(\mathrm{nucl})_{n-1}$ decreases and $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ increases with the number of fluoro atoms in the fluoroethylenes, but in the sum of these, the behavior of $E\mathrm{r}(\mathrm{nucl})_{n-1}$ predominates because this range of variation is about 0.6 eV, while the range for $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ is about 0.3 eV, resulting in the decrease of $E\mathrm{r}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ too. In accordance with Figure 11, the chloroethylenes suffer less effect in their energies as a consequence of the structure relaxation of the cation structure, and their AIPs values are closer to the VIPs, while the fluoroethylenes suffer more effects in their energies comparatively, and these effects are stronger as more fluoro atoms are added in the molecule. Therefore, the AIPs are more different than the VIP values for them.

Figure 12 shows the $\Delta \mathrm{ZPE}^{\mathrm{RN}}_{n-1,n-1}$ variation as a function of the number of halogen atoms. The values increase with the number of halogen atoms for the fluoroethylenes as they did for the chloroethylenes. As in $\Delta \mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$, the values are smaller than $E\mathrm{r}(\mathrm{nucl})_{n-1}$ and $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ and have little effect on the AIP values.

Finally, the AIP(G3) values as a function of the number of halogen atoms are shown in Figure 13. The AIP(G3) values are the sum of the VIP(G3) and $E\mathrm{r}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ values; therefore, for the fluoroethylenes, VIP(G3) is nearly constant, and $E\mathrm{r}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ decreases with the addition of halogen atoms. The AIP(G3) values decrease too. For the chloroethylenes, as the VIP(G3) and $E\mathrm{r}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ values decrease, AIP(G3) decreases in the same way. As in VIP(G3), the fluoroethylenes have higher values of AIP(G3) than the chloroethylenes.

Comparison with Previous Works. Since 1962, ionization potentials for haloethylenes have been calculated using ab initio

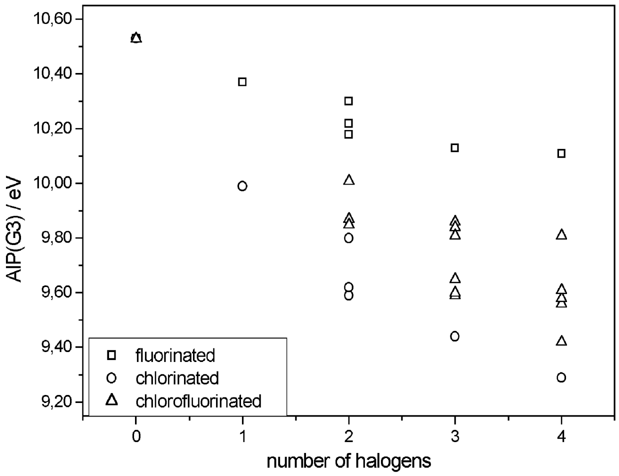

Figure 13. AIP(G3) as a function of the number of halogens (G3 theory results).

and density functional theory.[21,24−39] Table 4 shows VIPs and AIPs calculated after 1980[26−39] via elaborate calculations with several methods and basis sets allowed by the computer development. Thereby, the deviations from experimental data are, in the majority, higher when compared with ours at VIP(G*X*) and AIP(G*X*).

Now considering, in modulo, those and our calculated deviations from experimental data, the VIP of 10.56 eV for fluoroethylene (entry 41 in Table 4) obtained with one of the B3LYP[37] calculations has the same deviation from the experimental value as the VIP(G2) value and a deviation of 0.01 eV higher than the VIP(G3) value; for (*E*)-1,2-difluoroethylene, the SCF[35] value of 10.64 eV (entry 45 in Table 4) has 0.01 eV of deviation from the experimental data, the same deviation of the VIP(G2) and VIP(G3) values; for (*Z*)-1,2-difluoroethylene, the SCF[35] value of 10.64 (entry 54 in Table 4) has a smaller deviation by 0.01 eV than that of the VIP(G3) value and 0.02 eV smaller than that of the VIP(G2) value, and the B3LYP[37] value of 10.59 eV (entry 59 in Table 4) has the same deviation as the VIP(G3) value and a smaller deviation by 0.01 eV than the VIP(G2) value; for 1,1-difluoroethylene, the SCF[35] value of 10.74 eV (entry 63 in Table 4) has the same deviation as the VIP(G2) value and a higher deviation by 0.01 eV than the VIP(G3) value; the B3LYP[37] value of 10.64 eV (entry 68 in Table 4) has higher deviations by 0.2 and 0.3 eV than that of the VIP(G2) and VIP(G3) values, respectively; and finally, for trifluoroethylene, the MRDCI[34] value of 10.70 eV (entry 70 in Table 4) has a higher deviation by 0.02 eV than that of the VIP(G2) and VIP(G3) values, and the B3LYP[37] value of 10.56 eV (entry 77 in Table 4) has the same deviation as the VIP(G3) and VIP(G2) values.

Still, for AIPs, the values of 9.639 and 9.61 eV calculated by CCSD(T) and G3X[30] (entry 10 and 11, respectively, in Table 4) for (*E*)-1,2-dichloroethylene have no deviation from the experimental data, also like our results. For (*Z*)-1,2-dichloroethylene, the CCSD(T)[31] result (entry 15 in Table 4) has 0.02 eV of deviation for our G2 result and is 0.01 eV lower than our G3 result. All of the remaining calculated VIP and AIP data have higher deviations by 0.04 eV than the deviations of our calculated results.

Therefore, for quite all of our calculated results for the haloethylenes, the G2 and G3 methods quantitatively predict the closest values compared with the experimental data as opposed to the other previously utilized methods or, at least, values with the same exactness.

Conclusions

We have successfully achieved adiabatic and vertical ionization potential values for fluorinated, chlorinated, and chlorofluorinated ethylenes by the G2 and G3 theories. Our results are the closest values compared with available experimental data in the literature.

We achieved calculated VIP values with deviations from the experimental data in the range of 0.00−0.10 eV with G2 and G3 theory calculations, except for $CCl_2{=}CF_2$, whose deviation was 0.15 eV, indicating that the experimental value shall be re-examined. The average absolute deviation from the experimental data was 0.049 eV for the VIP(G2) results and 0.045 eV for the VIP(G3) results. Moreover, we have obtained VIP(G3) values for the following species not available in the literature (in eV): VIP ((*E*)-CHCl=CFCl) = 9.89, VIP ((*Z*)-CHCl=CFCl) = 9.90, VIP ((*E*)-CFCl=CHF)= 10.26, VIP ((*Z*)-CFCl=CHF) = 10.25, VIP ((*E*)-CFCl=CFCl) = 9.93, VIP ((*Z*)-CFCl=CFCl) = 9.96, VIP ($CCl_2{=}CFCl$) = 9.71, VIP ($CF_2{=}CHCl$) = 10.19, VIP ($CHF{=}CCl_2$) = 9.96, VIP ($CH_2{=}CFCl$) = 10.32, VIP ((*Z*)-CHCl=CHF) = 10.16, and VIP ((*E*)-CHCl=CHF) = 10.16.

The changes in the correlation energy and the relaxation energy of the orbitals are important to reach better quantitative results, as can be seen by the large range of deviations from the experimental data of the HOMO energy, $-\epsilon$, of 0.04−0.53 eV. Also, Koopmans's theorem fails to describe the behavior of the VIPs as a function of the number of fluoro atoms on the molecule of fluoroethylenes; therefore, the HOMO energy increases with the rising number of fluoro atoms, while the VIPs decrease initially and increase after the difluoroethylene isomers. However, Koopmans's theorem describes the behavior of chloroethylenes as the HOMO energy and the VIPs decrease as a function of the number of chloro atoms in the molecule, but the values obtained for VIP(G*X*) show a better agreement with the experimental data. For none of the chloroethylenes do Er_{n-1}^{CN} and $\Delta E(\text{corr})_{n,n-1}^{CN}$ cancel each other, as expected for Koopmans's theorem, giving the closest results to the experimental data (as occurs for the difluoroethylenes); however, for $CHCl{=}CH_2$, no agreement is found with this statement, and the HOMO energy is closer to the experimental data because its value is low.

$\Delta E(\text{corr})_{n,n-1}^{CN}$ varies in a large range of values compared to Er_{n-1}^{CN}, decreasing with the number of halogen atoms in the molecule, and this phenomenon is not accomplished by Koopmans's theorem. VIP(HF) behaves as the HOMO energy and shows the same failure of Koopmans's theorem in not taking into account $\Delta E(\text{corr})_{n,n-1}^{CN}$.

Our calculated values for the AIPs have deviations from the experimental data in the range of 0.00−0.04 eV for G2 and G3 theoretical calculations and average absolute deviations from the experimental values of 0.014 eV for G2 and 0.015 eV for G3. Moreover, we have obtained values, not available in the literature, for the following species using G3 theory (in eV): AIP ((*E*)-CHCl=CFCl) = 9.59, AIP ((*Z*)-CHCl=CFCl) = 9.60, AIP ($CCl_2{=}CFCl$) = 9.42, and AIP ($CHF{=}CCl_2$) = 9.65. Again, we suggest a review of the experimental data for (*E*)- and (Z)-1,2-dichloro-1,2-difluoroethylene isomers, with the objective to confirm if the single value in the literature is the correct one. Furthermore, the chloroethylenes have small variations in $Er(\text{nucl})_{n-1} + \Delta E(\text{corr})_{n-1,n-1}^{RN}$, and therefore, they have AIP values closest to the VIP values, as compared with the fluoroethylenes.

The variation of the zero-point energies, $\Delta ZPE_{n,n-1}^{CN}$ and $\Delta ZPE_{n-1,n-1}^{RN}$, are small when compared with the variation of

TABLE 4: Previously Calculated VIPs and AIPs from the Literature

entry	substance	method^{a}	VIP^{bc}/eV	AIP^{c}/eV
01	$CHCl=CH_2$	SCF^{d}	(K) 10.00 (−0.20)	
02		SCF^{e}	(Δ) 9.11 (−1.09)	8.76 (−1.23)
03		SDCI^{e}	(Δ) 9.79 (−0.41)	9.41^{f} (−0.58)
04		B3LYP^{g}	(Δ) 9.966 (−0.23)	
05		B3LYP^{g}	(H) 7.363 (−2.84)	
06		B3LYP^{g}	(H) 7.414 (−2.79)	
07	(*E*)-$CHCl=CHCl$	SCF^{d}	(K) 9.90 (0.10)	
08		SCF^{h}	(Δ) 9.10 (−0.70)	8.69 (−0.91)
09		SDCI^{h}	(Δ) 9.52 (−0.28)	9.10^{i} (−0.50) 9.09^{j} (−0.51)
10		CCSD(T)^{k}		9.639 (0.0)
11		G3X^{k}		9.61 (0.0)
12	(*Z*)-$CHCl=CHCl$	SCF^{d}	(K) 9.90 (0.10)	
13		SCF^{h}	(Δ) 9.09 (−0.71)	8.70 (−0.95)
14		SDCI^{h}	(Δ) 9.52 (−0.28)	9.11^{i} (−0.54) 9.10^{j} (−0.55)
15		CCSD(T)^{l}		9.668 (0.02)
16	$CCl_2=CH_2$	SCF^{d}	(K) 10.47 (0.47)	
17		SCF^{m}	(K) 10.60 (0.60)	
18		SCF^{m}	(K) 10.63 (0.63)	
19		SCF^{m}	(K) 10.29 (0.29)	
20		SCF^{h}	(Δ) 9.11 (−0.89)	8.71 (−1.08)
21		SDCI^{h}	(Δ) 9.64 (−0.36)	9.22^{i} (−0.57) 9.20^{j} (−0.59)
22		B3LYP^{g}	(Δ) 9.805 (0.19)	
23		B3LYP^{g}	(H) 7.432 (−2.57)	
24		B3LYP^{g}	(H) 7.456 (−2.54)	
25	$CCl_2=CHCl$	SCF^{d}	(K) 10.15 (0.55)	
26		SCF^{e}	(Δ) 9.06 (−0.54)	8.65 (−0.80^{n})
27		SDCI^{e}	(Δ) 9.39 (−0.21)	8.96^{f} (−0.49^{n})
28	$CCl_2=CCl_2$	SCF^{d}	(K) 10.06 (0.56)	
29		SCF^{o}	(Δ) 9.02 (−0.48)	8.61 (−0.71)
30		SDCI^{o}	(Δ) 9.23 (−0.27)	8.81^{i} (−0.51) 8.79^{j} (−0.53)
31	$CH_2=CHF$	MRDCI^{p}	(Δ) 9.96 (−0.67)	
32		SCF^{q}	(K) 10.58 (0.21)	
33		SCF^{q}	(K) 10.48 (0.11)	
48		SCF^{t}	(Δ) 9.38 (−1.25)	8.84 (−1.31^{n})
49		SDCI^{t}	(Δ) 9.90 (−0.73)	9.41^{i} (−0.74^{n}) 9.40^{j} (−0.75^{n})
50		B3LYP^{s}	(Δ) 10.49 (−0.14)	10.04^{i} (−0.11^{n}) 10.05^{j} (−0.10^{n})
51		MP2^{s}	(Δ) 10.45 (−0.18)	10.00 (−0.15^{n})
52	(*Z*)-$CHF=CHF$	MRDCI^{p}	(Δ) 10.12 (−0.50)	
53		SCF^{q}	(K) 10.84 (0.22)	
54		SCF^{q}	(K) 10.64 (0.02)	
55		SCF^{r}	(K) 11.22 (0.60)	
56		SCF^{r}	(Δ) 10.21 (−0.41)	
57		SCF^{t}	(Δ) 9.38 (−1.24)	8.85 (−1.35^{n})
58		SDCI^{t}	(Δ) 9.90 (−0.72)	9.42^{i} (−0.78^{n}) 9.41^{j} (−0.79^{n})
59		B3LYP^{s}	(Δ) 10.59 (−0.03)	10.08^{f} (−0.12^{n})
60		MP2^{s}	(Δ) 10.46 (−0.16)	10.02 (−0.18^{n})
61	$CF_2=CH_2$	MRDCI^{p}	(Δ) 10.19 (−0.51)	
62		SCF^{q}	(K) 10.95 (0.25)	
63		SCF^{q}	(Δ) 10.74 (0.04)	
64		SCF^{r}	(K) 11.37 (0.67)	
65		SCF^{r}	(Δ) 10.31 (−0.39)	
66		SCF^{t}	(Δ) 9.41 (−1.29)	8.88 (−1.42)
67		SDCI^{t}	(Δ) 9.99 (−0.71)	9.52^{i} (−0.78) 9.51^{j} (−0.79)
68		B3LYP^{s}	(Δ) 10.64 (−0.06)	10.23^{i} (−0.07) 10.22^{j} (−0.08)
69		MP2^{s}	(Δ) 10.54 (−0.16)	10.10 (−0.20)
70	$CF_2=CHF$	MRDCI^{p}	(Δ) 10.70 (0.08)	
71		SCF^{q}	(K) 11.17 (0.55)	
72		SCF^{q}	(K) 10.85 (0.23)	
73		SCF^{r}	(K) 11.68 (1.06)	
74		SCF^{r}	(Δ) 10.70 (0.08)	
75		SCF^{e}	(Δ) 9.55 (−1.07)	8.90 (−1.24)
76		SDCI^{e}	(Δ) 9.91 (−0.71)	9.35^{i} (−0.79) 9.36^{j} (−0.78)
77		B3LYP^{s}	(Δ) 10.56 (−0.06)	10.04^{i} (−0.10) 10.06^{j} (−0.08)

TABLE 4 (Continued)

entry	substance	method[a]	VIP[bc]/eV	AIP[c]/eV
34		SCF[r]	(K) 10.79 (0.16)	
35		SCF[r]	(Δ) 9.72 (−0.91)	
36		SCF[e]	(Δ) 9.22 (−1.41)	8.83 (−1.54)
37		SDCI[e]	(Δ) 9.99 (−0.64)	9.60[f] (−0.77)
38		B3LYP[g]	(Δ) 10.464 (−0.17)	
39		B3LYP[g]	(H) 7.532 (−3.10)	
40		B3LYP[g]	(H) 7.615 (−3.01)	
41		B3LYP[s]	(Δ) 10.56 (−0.07)	10.23[i] (−0.14) 10.21[j] (−0.16)
42		MP2[s]	(Δ) 10.51 (−0.12)	10.16 (−0.21)
43	(*E*)-CHF═CHF	MRDCI[p]	(Δ) 10.19 (−0.44)	
44		SCF[q]	(K) 10.84 (0.21)	
45		SCF[q]	(K) 10.64 (0.01)	
46		SCF[r]	(K) 11.19 (0.56)	
47		SCF[r]	(Δ) 10.18 (0.45)	
78		MP2[s]	(Δ) 10.50 (−0.12)	9.98 (−0.16)
79	$CF_2═CF_2$	MRDCI[p]	(Δ) 9.92 (−0.77)	
80		SCF[q]	(K) 11.48 (0.86)	
81		SCF[q]	(K) 11.05 (0.36)	
82		SCF[r]	(K) 12.0 (1.31)	
83		SCF[r]	(Δ) 11.2 (0.58)	
84		SCF[u]	(Δ) 9.74 (−0.95)	8.99 (−1.11[n])
85		SDCI[u]	(Δ) 10.32 (−0.37)	9.67[f] (−0.43[n])
86		B3LYP[g]	(Δ) 10.537 (−0.15)	
87		B3LYP[g]	(H) 7.627 (−3.06)	
88		B3LYP[g]	(H) 7.575 (−3.12)	
89		B3LYP[s]	(Δ) 10.60 (−0.09)	10.03[i] (−0.07[n]) 10.06[j] (−0.04[n])
90		MP2[s]	(Δ) 10.55 (−0.14)	9.97 (0.13[n])

[a] For basis set details, see the respective reference to each result. [b] K: HOMO value in accordance with Koopmans's theorem. Δ: value obtained by the difference between the energies of the charged and neutral substance, keeping the geometry of the neutral one. H: HOMO energy (Koopmans's theorem is not valid). [c] Value in parentheses is the difference between the calculated value and the experimental data. [d] Ref 26. [e] Ref 27. [f] The values with and without ZPE correction are the same. [g] Ref 28. [h] Ref 29. [i] Value without ZPE correction. [j] Value with ZPE correction. [k] Ref 30. [l] Ref 31. [m] Ref 32. [n] Value obtained in reference to the smaller experimental data shown in Table 1. [o] Ref 33. [p] Ref 34. [q] Ref 35. [r] Ref 36. [s] Ref 37 VIP value closest to the experimental data among several calculated ones. [t] Ref 38. [u] Ref 39.

the correlation and relaxation energies and do not significantly affect the final calculated results of the VIPs and AIPs.

Besides this, VIP and AIP values are higher for the fluoroethylenes than for the chloroethylenes species. However, as one can seen, the different behavior of the chloroethylenes and the fluoroethylenes as a function of the halogen atoms occurs markedly for the VIPs, whose values increase for the fluoroethylenes, while a decrease occurs for the chloroethylenes. AIP values for the fluoroethylenes decrease with a rising number of fluoro atoms in the molecule, and this behavior is caused by the $Er(\mathrm{nucl})_{n-1}$ value. The AIPs of the chloroethylenes have the same behavior as the VIPs, decreasing with the number of chloro atoms.

In addition, the results for the chlorofluoroethylenes behave as a mixture of the chloroethylenes and the fluoroethylenes because the calculated values lie between those for these two groups of compounds.

Also, the difficulty in achieving the correct structure for the ethylene cation using the G2 and G3 theories may be taken as a warning for someone to be alert to unexpected results caused by the methodology and the basis set applied in the calculations. As B3LYP calculations give the correct structure, it would be more reliable the use of the G3X[40] theory to achieve a better result for the ethylene.

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Supporting Information Available: Energies obtained at G2 and G3 theories, ZPE and Hartree−Fock energies of all neutral and charged substances; experimental ionization potentials; results with G2 theory for $-\epsilon$, Er^{CN}_{n-1}, $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, $\Delta\mathrm{ZPE}^{\mathrm{CN}}_{n,n-1}$, VIP(G$X$), $Er(\mathrm{nucl})_{n-1}$, $\Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$, $\Delta\mathrm{ZPE}^{\mathrm{RN}}_{n-1,n-1}$, AIP(G2), $Er^{\mathrm{CN}}_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, and $Er(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})^{\mathrm{RN}}_{n-1,n-1}$ as a function of number of halogens; and the dependence between VIP(G2) and $-\epsilon$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Yamazaki, I.; Miki, N.; Uesugi, H. Jpn. Patent 107968, 2002; *Chem. Abstr.* **2002**, *136*, 1490.

(2) Ishida, K.; Mohammad, R. I. Jpn. Patent 258495, 2002; *Chem. Abstr.* **2002**, *137*, 1534.

(3) Song, W. J.; Yang, J. H. EP Patent, 278244A2, 2003; *Chem. Abstr.* **2003**, *138*, 1658.

(4) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(5) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(6) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(7) Koopmans, T. *Physica* **1933**, *1*, 104.

(8) Minkin, V. I. *Pure Appl. Chem.* **1999**, *71*, 1919.

(9) Jensen, F. *Introduction to Computational Chemistry*; John Wiley and Sons: Chichester, U.K., 1999; p 64.

(10) Levine, I. N. *Quantum Chemistry*, 5th ed; Prentice Hall: Engelwood Cliffs, NJ, 2000; p 503.

(11) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley and Sons: Chichester, U.K., 1986; p 24.

(12) Maksić, Z. B.; Vianello, R. *J. Phys. Chem. A* **2002**, *106*, 6515.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(15) Koppel, H.; Domcke, W.; Cederbaum, L. S.; Vonniessen, W. *J. Chem. Phys*. **1978**, *69*, 4252.

(16) Abrams, M. L.; Valeev, E. F.; Sherrill, C. D.; Crawford, T. D. *J. Phys. Chem. A* **2002**, *106*, 2671.

(17) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17* (supplement 1).

(18) Lias, S. G.; Levin, R. D.; Kafafi, S. A. NIST Chemistry WebBook. http://webbook.nist.gov (June 2005), In *Ion Energetics Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD.

(19) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. NIST Chemistry WebBook. http://webbook.nist.gov (June 2005), In *Ion Energetics Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD.

(20) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. NIST Chemistry WebBook. http://webbook.nist.gov (June 2005), In *Ion Energetics Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD.

(21) Pappas, J. A. *THEOCHE*, **1974**, *22*, 69.

(22) Curtiss, L. A.; Raghavachari, K.; Redefern, P. C.; Pople, J. A. *J. Chem. Phys*. **2000**, *112*, 7374.

(23) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys*. **2005**, *123*, 124107.

(24) Favini, G. *Gazz. Chim. Ital.* **1962**, *92*, 244.

(25) Meza, S.; Wahlgren, U. *Theor. Chim. Acta* **1971**, *21*, 323.

(26) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S.; *Handbook of HeI Photoelectron Spectra of Fundamental Organic Coumpounds*; Japan Scientific Society: Tokyo, Japan, 1981.

(27) Takeshita, K. *Theor. Chem. Acc*. **1999**, *101*, 343.

(28) Zhan, C.; Nichols, J. A.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 4184.

(29) Takeshita, K. *J. Chem. Phys*. **1999**, *110*, 6792.

(30) Woo, H. K.; Wang, P.; Lau, K. C.; Xing, X.; Ng, C. Y. *J. Phys. Chem. A* **2004**, *108*, 9637.

(31) Lau, K. C.; Woo, H. K.; Wang, P.; Xing, X.; Ng, C. Y. *J. Chem. Phys*. **2006**, *124*, 224311.

(32) Chuaqui, M. H.; Mei, L.; Mathers, C. P.; Allison, M. L.; Ying, J. F.; Leung, K. T. *J. Chem. Phys.* **1995**, *102*, 90.

(33) Takeshita, K. *J. Chem. Phys*. **1995**, *102*, 8922.

(34) Beckmann, H. O.; Brawn, W.; Jochims, H. W.; Ruhl, E.; Baumgartel, H. *Chem. Phys. Lett.* **1985**, *121*, 499.

(35) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc*. **1986**, *108*, 1585.

(36) Heaton, M. M.; El-Talbi, M. R. *J. Chem. Phys.* **1986**, *85*, 7198.

(37) Wen-Zuo, L.; Ming-Bao, H. *Acta Phys. Chim. Sin*. **2004**, *20*, 21.

(38) Takeshita, K. *Chem. Phys*. **1999**, *250*, 113.

(39) Takeshita, K. *Theor. Chim. Acta* **1996**, *93*, 243.

(40) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys*. **2001**, *114*, 108.