THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

Electronic Properties of Chlorine, Methyl, and Chloromethyl as Substituents to the Ethylene Group—Viewed from the Core of Carbon

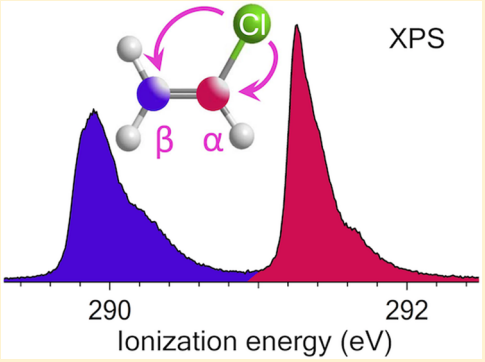
Maria G. Zahl,[†] Randi Fossheim,[†] Knut J. Børve,*[,†] Leif J. Sæthre,[†] and T. Darrah Thomas[‡]

[†]Department of Chemistry, University of Bergen, NO-5007 Bergen, Norway

[‡]Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, United States

Supporting Information

ABSTRACT: "Substituent effects" is an important and useful concept in organic chemistry. Although there are many approaches to parametrizing the electronic and steric effects of substituents, the physical basis for the parameters is often unclear. The purpose of the present work is to explore the properties of chemical shifts in carbon 1s energies as a well-defined basis for characterizing substituents to an ethylene C═C moiety. To this end, high-resolution carbon 1s photoelectron spectra of six chloro-substituted ethenes and seven chloro-substituted propenes have been measured in the gas phase. Site-specific adiabatic ionization energies have been determined from the spectra using theoretical *ab initio* calculations to predict the vibrational structures. For two molecules, 3-chloropropene and 2,3-dichloropropene, the spectral analyses give quantitative results for the conformer populations. The observed shifts have been analyzed in terms of initial-state (potential) and relaxation effects, and charge relaxation has also been analyzed by means of natural resonance theory. On the basis of core-level spectroscopy and models, chlorine, methyl, and chloromethyl have been characterized in terms of their effect on the carbon to which they are attached (α site) as well as the neighboring sp^2 carbon (β site). The derived spectroscopic substituent parameters are characterized by both inductive (electronegativity) effects and the ability of each substituent to engage in electron delocalization via the π system. Moreover, the adopted approach is extended to include substituent−substituent interaction parameters.



INTRODUCTION

Chlorine takes on many and diverse roles as a substituent of considerable importance in organic chemistry. It may provide or contribute to the desired molecular functionality, chemical stability and also solubility or interfacial properties. Additionally, chlorine may activate or deactivate neighboring functional groups and thereby tune reactivity or simply provide a site for further functionalization. This broad area of application is made possible by chlorine's diverse electronic properties as being electron-withdrawing, polarizable, and able to donate electrons to a neighboring π-system.

Different reactions may be responsive to different aspects of a substituent, and the interplay between the demands of a particular chemical transformation and the nature of the substituent is compactly and conveniently summarized in linear free-energy relationships, Hammett's equation being the best known example. In these models, each substituent is described by one or several parameters that are associated with specific aspects of electronic influence, such as the inductive capacity or through-space action by way of an electrostatic field, possibly augmented by a designated steric parameter.[1] Even when predictions made from linear free-energy relationships do not agree with observations, they may give useful indications of departure from additivity, e.g., strong interaction between two or more substituents such as exemplified by *p*-nitroaniline.[2]

Substituent parameters are usually determined from fitting the underlying equation to vast amounts of empirical reactivity and their precise physical interpretation may be uncertain. It would clearly be advantageous to characterize substituents in terms of physiochemical properties that are directly measurable or at least computable. X-ray photoelectron spectroscopy (XPS) offers an interesting alternative because this technique is able to probe the electronic structure of specific atoms in a molecule while at the same time being sensitive to many of the electronic properties of substituents, including electronegativity and polarizability. Moreover, the high resolution now attainable at third- and fourth-generation synchrotrons in conjunction with modern electron analyzers makes it possible to assign individual 1s ionization energies to all functionalized carbon atoms in rather complex organic molecules, thus allowing direct probing at the reactive sites.

Received: June 9, 2015
Revised: August 6, 2015
Published: August 17, 2015

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

The relationship between Hammett parameters and XPS energies has been a research topic since 1976[3] and it has been established that C 1s energies correlate well with Hammett $\sigma_{m/p}$ values (but not σ^+).[3−5] A different and still closely related approach adopted in the present work is to characterize substituents directly in terms of their local and more distant effects on core ionization energies. This line of attack has the attractive feature that it opens for direct assessment of the mutual interaction of substituents.

Starting from an early XPS study[6] of monohalogenated ethenes and ethanes, the aim of the present work is to use carbon 1s ionization energies to explore the substituent effects of chlorine on the ethylene (C═C) moiety, including nonadditivity effects involving either two Cl substituents or a Cl substituent together with either CH_3 or CH_2Cl. Carbon 1s photoelectron spectra of 13 chlorinated ethenes and propenes are recorded and analyzed by means of theoretical vibrational line shapes to obtain accurate ionization energies. Initial- and final-state contributions to the ionization energies have been analyzed by means of *ab initio* calculations. As a further demonstration of the sensitivity of ionization energies to the chemical environment, the C 1s photoelectron spectra for 3-chloropropene and 2,3-dichloropropene, both of which possess two thermally accessible rotamers, were analyzed to obtain the corresponding conformational populations.

METHODS

Experimental Procedures. Gas phase carbon 1s spectra were measured at beamline I411 at MAX-lab[7,8] and at beamline 10.0.1 at the ALS[9] using a photon energy of 330 eV. Photoelectrons were analyzed with Scienta SES-200 hemispherical electron analyzers. Absolute calibration of the ionization energy scale was achieved by measuring a mixture of sample and carbon dioxide, using the accurately known adiabatic ionization energy of CO_2 (297.664(30) eV[10]). Moreover, because the details of the CO_2 spectrum are well-known, including lifetime width and vibrational fine structure,[11] this allows the instrumental broadening to be determined from a fit to the CO_2 spectrum. Assuming a Gaussian function for the instrumental broadening, the full width at half-maximum (fwhm) was found to be in the range 60−80 meV, except for 3-chloropropene for which it was 90 meV.

Franck−Condon Factors and Single-Point Energy Calculations. To assist in the analysis of the carbon 1s photoelectron spectra, Franck−Condon vibrational line shapes were computed for each unique carbon atom and used in fits to the experimental spectra. To this end, molecular geometries were optimized for the neutral and ionized electronic ground states, and the normal mode vectors and harmonic frequencies were determined for each species. The final Franck−Condon model employed normal modes and scaled frequencies obtained with B3LYP, combined with geometry changes computed at the CCSD(T) level of electronic-structure theory. In these calculations, carbon and hydrogen were represented by Dunning triple-ζ bases[12] plus single sets of polarization functions (p for H, d for C).[13] Chlorine was described using the triple-ζ basis set of McLean and Chandler[14] augmented with a double polarization set by splitting the original[15] single d exponent (α = 0.75) into 2α = 1.50 and $\alpha/2$ = 0.375.[16] This basis set will be referred to as the tzp basis. For core-ionized carbon, the corresponding nitrogen basis was used with all exponents scaled by a factor of 0.9293.[17] To represent the core of the ionized atom, the effective core potential (ECP) by Stevens et al.[18] was scaled to account for only one electron in the 1s shell.[19] Several of the propenes undergo rather large internal rotation about the C2−C3 bond following ionization and, because of the anharmonic nature of the associated rotational potentials, the accompanying vibrational excitation was obtained in the 1-D hindered-rotor approximation.[20] A detailed account of methods and procedures used to form Franck−Condon profiles is provided as Supporting Information.

Theoretical shifts in C 1s ionization energies were computed using a selection of models of different sophistication. In addition to the tzp bases described above, correlation-consistent bases of cardinal numbers three and four were used. The first of these will be denoted (aug-)TZ and is defined by the following components: H, cc-pVTZ;[21] C, cc-pCVTZ;[21] Cl, aug-cc-pV(T+d)Z.[22] The second combination of correlation-consistent bases is denoted (aug-)QZ and consists of H, cc-pVQZ;[21] C, cc-pCVQZ;[21] and Cl, aug-cc-pCVQZ.[23,24] Single-point energies were evaluated with B3LYP in the B3LYP/tzp-optimized geometries, and MP2, MP4(SDQ), and CCSD(T) in geometries optimized with CCSD(T)/tzp. In all adiabatic energies, zero-point vibrational corrections were included as calculated using B3LYP/tzp.

It is frequently useful to analyze a core-level ionization energy (IE) in terms of contributions from the charge distribution in the neutral ground-state molecule (the initial-state contribution, V) and charge reorganization in the ion (relaxation, R), such that IE = $V - R$. According to Koopmans theorem, the first term may be approximated by the negative of the Hartree−Fock energy of the core orbital. To include also electron correlation, an extended version of Koopmans theorem (EKT) was developed.[25] As applied to shifts in ionization energies, the appropriate expression reads $\Delta\mathrm{EKT} = -\Delta\epsilon_c + \Delta\,(U^{\mathrm{corr}} - U^{\mathrm{HF}})$, where ϵ_c is the orbital energy and U is the electrostatic potential at the site of ionization, superscripted to indicate the level of electronic-structure theory used for evaluation. Thus, U^{corr} denotes the potential as evaluated from a correlated electron density, which in this work was obtained in an MP4(SDQ) calculation. The relaxation contribution to the chemical shift, ΔR, was obtained as the difference between ΔEKT and the experimental shift and is believed to be accurate to 0.03 eV.

All calculations were performed using the Gaussian set of programs (G03 and G09)[26] except for a set of Hartree−Fock/tzp calculations carried out to explore the validity of the ECP model for core-ionized chloroethenes, which were conducted with the Dalton package of programs.[27]

Fitting Models. To determine accurate adiabatic energies, line-shape profiles representing the contribution from each of the symmetry-unique carbon atoms are fit to the recorded spectra. These profiles include vibrational structure through Franck−Condon distributions (for details, see above) and various contributions to line broadening. More specifically, the vibrational line shape was convoluted with a Gaussian function representing the experimental broadening and with the asymmetric function of van der Straten et al.[28] representing the combined effects of lifetime broadening and postcollision interaction between the Auger electron and the photoelectron. The lifetime width (fwhm) was fixed to 100 meV for nonchlorinated carbons.[11,29] This was reduced by 10 meV per chlorine directly attached to the carbon atom in question, on the basis of a recent study of lifetime broadening in the chloromethanes.[30]

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Table 1. Experimental Adiabatic C 1s Ionization Energies (IE, eV) and Experimental and Theoretical Shifts in Adiabatic IE Relative to that of Ethene (ΔIE, eV)

compound	carbon	IE, exp	ΔIE,[a] exp	ΔIE, calc		ΔEKT[b]
				CCSD(T)	MP4(SDQ)	
propene	C1	290.136(30)[c]	−0.559(20)	−0.572	−0.584	−0.283
	C2	290.612(30)[c]	−0.083(20)	−0.083	−0.080	0.149
	C3	290.671(30)[c]	−0.024(20)	−0.061	−0.049	−0.153
chloroethene	C1	292.203(30)	1.508(20)	1.524	1.543	1.923
	C2	290.744(30)	0.049(20)	0.033	0.037	0.481
cis-1,2-dichloroethene		292.148(30)	1.453(20)	1.458	1.480	2.231
trans-1,2-dichloroethene		292.162(40)	1.467(30)	1.495	1.512	2.284
1,1-dichloroethene	C1	293.516(30)[d]	2.821(20)[d]	2.881	2.915	3.585
	C2	290.761(30)[d]	0.066(20)[d]	0.054	0.058	0.812
trichloroethene	C1	293.428(30)	2.733(20)	2.786	2.815	3.846
	C2	292.138(30)	1.443(20)	1.459	1.474	2.513
tetrachloroethene		293.435(40)	2.740(30)	2.759	2.781	4.071
cis-1-chloropropene	C1	291.626(30)	0.930(20)	0.970	0.974	1.616
	C2	290.666(30)	−0.029(20)	0.001	0.009	0.620
	C3	290.782(30)	0.087(20)	0.057	0.075	0.113
trans-1-chloropropene	C1	291.619(30)	0.924(20)	0.970	0.980	1.554
	C2	290.663(30)	−0.032(20)	−0.004	0.009	0.540
	C3	290.949(30)	0.254(20)	0.230	0.251	0.226
2-chloropropene	C1	290.304(30)	−0.391(20)	−0.424	−0.432	0.221
	C2	292.100(30)	1.405(20)	1.448	1.469	2.048
	C3	291.081(30)	0.386(20)	0.324	0.340	0.377
3-chloropropene, *gauche*	C1	290.496(30)	−0.199(20)	−0.123	−0.128	0.346
	C2	290.949(30)	0.254(20)	0.294	0.296	0.661
	C3	292.201(30)	1.506(20)	1.520	1.545	1.894
3-chloropropene, *syn*	C1	290.355(30)	−0.340(20)	−0.319	−0.325	0.100
	C2	290.885(30)	0.190(20)	0.226	0.233	0.611
	C3	292.204(30)	1.509(20)	1.557	1.580	1.925
1,1-dichloropropene	C1	292.963(30)	2.268(20)	2.347	2.363	3.274
	C2	290.747(30)	0.052(20)	0.054	0.060	0.956
	C3	290.948(30)	0.253(20)	0.229	0.248	0.385
cis-1,3-dichloropropene	C1	291.998(30)	1.303(20)	1.360	1.375	2.168
	C2	290.986(30)	0.291(20)	0.305	0.315	1.058
	C3	292.275(30)	1.580(20)	1.578	1.615	2.097
2,3-dichloropropene, *anti*	C1	290.472(30)	−0.223(20)	−0.212	−0.215	0.542
	C2	292.323(30)	1.628(20)	1.692	1.716	2.428
	C3	292.550(30)	1.855(20)	1.872	1.900	2.363
2,3-dichloropropene, *gauche*	C1	290.596(30)	−0.099(20)	−0.051	−0.055	0.745
	C2	292.397(30)	1.702(20)	1.737	1.756	2.438
	C3	292.512(30)	1.817(20)	1.814	1.846	2.304

[a]Experimental energies relative that of ethene, 290.695 eV.[10] [b]ΔEKT = relative extended Koopmans theorem energies, at the MP4(SDQ) level. [c]From ref 33. [d]From ref 34.

Equipped with these line-shape profiles, energy positions and intensities of each peak as well as a constant background were determined in least-squares fits to the observed spectra by means of the SPANCF fitting package.[31,32] Adiabatic ionization energies were defined from the position of the 0−0 vibrational line in each case, whereas the corresponding vertical ionization energy is formed from the adiabatic energy by adding the average vibrational energy from the computed Franck−Condon profile.

RESULTS AND DISCUSSION

The first part of this section is devoted to establishing accurate carbon 1s energies for 13 chlorinated ethenes and propenes. Naming of compounds and numbering of carbon atoms (C1−C3) follow IUPAC conventions, as illustrated in Table S1 in the Supporting Information. For 1,2-dichloroethene and 1-chloropropene, both *cis* and *trans* isomers are considered, partly to decide whether geometric isomerism should be part of the subsequent analysis of substituent effects. Two other compounds, 3-chloropropene and 2,3-dichloropropene, possess two low-energy rotamers each and thus exist in conformational equilibria. To determine reliable ionization energies and also look for through-space interaction between substituents, the spectral analysis aims to determine conformer-specific ionization energies and, as added benefit, conformational populations.

The C 1s ionization energies are subsequently used to assess how chlorine affects the carbon−carbon double bond as well as how the effect of chlorine is modified by the presence of either another chlorine or either of two other substituents: CH_3 and CH_2Cl. The level of analysis is increased by decomposing the chemical shifts in ionization energies into contributions due to substituent modification in the neutral, ground-state molecule,

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Table 2. Errors in Theoretical Shifts (meV) in Adiabatic Carbon 1s Ionization Energies Relative to that of Ethene

method:	B3LYP	CCSD(T)		MP4(SDQ)		MP2
basis:	tzp	tzp	(aug-)TZ	(aug-)TZ	(aug-)QZ	(aug-)QZ
mean error	53	116	18	31	41	82
mean absolute error	65	117	31	31	50	99
root mean squared error	81	132	37	48	59	123
max error	161	235	79	95	120	284
measured ionization energies fitted to theoretical energies						
slope	0.952(6)	0.955(7)	0.984(5)	0.975(4)	0.966(4)	0.927(8)
intercept	−10(8)	−73(10)	−4(6)	−9(6)	−11(6)	−15(11)
root mean squared deviation	40	47	30	27	28	56

Table 3. Vertical Carbon 1s Ionization Energies (IE_v, in eV)

			ΔIE_v[a]			
compound	carbon	exp IE_v (this work)	exp	calc[b]	exp IE_v[36]	ΔIE_v[a,36]
chloroethene	C1	292.29(3)	1.47	1.50	292.35(7)	1.53
	C2	290.93(3)	0.11	0.13	290.99(7)	0.17
cis-1,2-dichloroethene		292.27(3)	1.45	1.49	292.31(7)	1.49
trans-1,2-dichloroethene		292.34(5)	1.52	1.55	292.41(7)	1.59
1,1-dichloroethene	C1	293.56(3)	2.74	2.81	293.62(7)	2.80
	C2	290.99(3)	0.17	0.17	290.93(7)	0.11
trichloroethene	C1	293.53(3)	2.71	2.78	293.58(7)	2.76
	C2	292.29(3)	1.47	1.52	292.39(7)	1.57
tetrachloroethene		293.51(5)	2.69	2.77	293.64(7)	2.82

[a]Relative to the vertical ionization energy of ethene of 290.823(30) eV.[10] [b]Calculated using CCSD(T)/(aug-)TZ.

on one hand, and substituent-effects on the rearrangement of charge following the ionization event, on the other.

Carbon 1s Ionization Energies. Carbon 1s X-ray photoelectron spectra have been recorded with instrumental broadening (fwhm) of 90 meV or better, for the following compounds: Ethene, chloroethene, *cis*- and *trans*-1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, tetrachloroethene, *cis*- and *trans*-1-chloropropene, 2- and 3-chloropropene, and 1,1-, *cis*-1,3-, and 2,3-dichloropropene. Representative examples and corresponding theory-based fitting models are shown in Figures 1 and 3, with the remaining spectra included as Supporting Information. The spectrum of 1,1-dichloroethene has been published previously[34] and is included here for completeness.

Adiabatic experimental ionization energies are listed in Table 1 as obtained from spectral analyses based on Franck−Condon vibrational profiles as described in the Methods. Also included in Table 1 are experimental chemical shifts (relative to ethene), with corresponding theoretically predicted shifts computed with two high-level electronic-structure methods (CCSD(T), MP4(SDQ)) in conjunction with large basis sets, (aug-)TZ. Although these are compared in some detail in the next section, it is noted that the agreement between our experimental and best theoretical shift data is highly satisfactory. As the theoretical energies may include systematic but not stochastic errors, the root-mean-squared deviation (RMSD) of the experimental values about the best-fit line between the two sets may be used to estimate the standard deviation in our experimental relative ionization energies. Such an analysis indicates that the experimental shifts in adiabatic energies are correct to better than 0.03 eV. However, the value of 0.03 eV is an upper limit as it may still contain contributions from systematic errors in the theoretical shift values beyond what can be corrected for by a linear fit. In ref 35, an analysis similar to the one discussed here was conducted on the basis of 77 C 1s energies from a diverse set of unsubstituted and fluorinated hydrocarbons. A total of 33 of the 77 energies correspond to sp^2-hybridized carbons. When compared to theoretical shifts computed at the CCSD(T)/cc-pVTZ level of theory, an RMSD deviation of 33 meV was obtained, agreeing closely with the present value of 30 meV obtained with CCSD(T)/(aug-)TZ. However, switching to tzp bases reduced the RMSD value to 21 meV, which then affords a tighter upper limit to the experimental uncertainty. This is a strong indication that 0.02 eV is a viable estimate of the experimental uncertainty also in the present shift data, although, as discussed below, the tzp set is not fit for accurate shift calculations for chlorinated compounds.

Vertical ionization energies, on the contrary, are formed from the adiabatic ionization energies by adding average vibrational excitation energies as computed from the theoretical vibrational profiles. This process may introduce additional errors in the vertical energies subject to the quality of our vibrational profiles, as will be addressed in a subsequent section.

Theoretical Shifts in Ionization Energies. In addition to the theoretical shifts in C 1s energies included in Table 1, the corresponding data computed with other combinations of electronic-structure methods and basis sets are provided as Supporting Information. Table 2 presents statistical analysis of the agreement between our computed shifts in C 1s energies and those obtained experimentally. The largest errors are obtained with the presumptively most accurate electronic-structure method, namely CCSD(T). The problem clearly lies in the basis set, tzp, and more specifically, in the chlorine part of this basis set. Switching to B3LYP, which is less demanding with respect to basis sets, almost halves the mean absolute error. The best agreement between computed and experimental chemical shifts is obtained with CCSD(T) in conjunction with

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

the (aug-)TZ basis, for which the root-mean-squared-error and the mean absolute error are down to 0.04 and 0.03 eV, respectively. MP4(SDQ) also provides very satisfactory accuracy with this basis, but improving the basis set to (aug-)QZ actually increases the two quoted error statistics to 0.06 and 0.05 eV. However, the two MP4(SDQ)-based models give the same accuracy as CCSD(T)/(aug-)TZ if used in linear fits to predict the chemical shift. The root-mean-squared-deviation of the prediction is 0.03 eV in all three cases.

It should be noted that the theoretical shift data are computed with the 1s-ionized carbon core represented by an effective core potential. This approximation constitutes a source of errors in the computed shifts which in the case of sp^2-hybridized carbon atoms in pure hydrocarbons were found to average below 0.01 eV at the HF/tzp level.[35] When the corresponding errors in computed ionization energies of the chloroethenes were explored by conducting proper hole-state calculations at the HF/(aug-)TZ level of theory, slightly larger errors were found for the chlorinated compounds and varying from 0 to 44 meV. Surprisingly, the largest deviations were found for two of the nonchlorinated carbons (C2 in chloroethene and 1,1-dichloroethene).

Vertical Ionization Energies for the Chloroethenes. For the chlorinated ethenes, vertical ionization energies with a quoted uncertainty of 0.07 eV are available in the literature.[36] These values are summarized in Table 3 for comparison with our values, most of which have estimated uncertainties of 0.03 eV. Generally, the two sets of ionization energies agree well and within the combined error bars, although with our values systematically lower by 0.07 eV on average and approaching twice this value in two instances.

It is unknown whether the results reported in ref 36 included recoil corrections. Under the conditions of the experiment, which involved Al Kα radiation, omitting the recoil corrections would make the reported vertical ionization energies for the chloroethenes too high by 0.04−0.05 eV. This is presumably the main source of discrepancy between the two sets of ionization energies. Additionally, the results of ref 36 were calibrated against Ar $2p_{3/2}$ (248.62 eV) whereas our calibration is based on a value of 248.629 eV for this line.[10] This difference is seen to increase the discrepancy of the two sets of data, but by only 0.01 eV.

The two cases of largest difference to ref 36 are the C2 energies in trichloroethene and tetrachloroethene. The trichloroethene case is instructive as this molecule contains two inequivalent carbon atoms and thus an intramolecular chemical shift that is independent of the calibration line and also recoil corrections. We get a value of 1.24 eV for this shift, compared to 1.19 eV in ref 36. From the preceding section, it follows that our value for the internal shift is prepared from the corresponding adiabatic shift, which is probably good to 0.02 eV or better, by adding the difference in mean vibrational excitation energy between the C1 and C2 peaks. To explore the possibility of increased errors due to the latter term, we made two independent determinations of the vibrational shift. First, the spectrum was refitted using a second set of Franck−Condon models prepared from geometries, frequencies, and normal modes obtained at the MP4(SDQ)/tzp level of theory and with normal modes expressed in internal rather than Cartesian coordinates. Second, a purely empirical fit was made to the experimental spectrum, and mean peak positions were found as weighted means over the Voigt lines contributing to each peak. In either case, the internal C1−C2 shift changed by 0.01 eV or less from our original values as included in Table 3. We conclude that our vertical energies are probably correct to the uncertainties given in the table.

Our vertical ionization energy for C2 in 1,1-dichloroethene is the only entry that is larger than reported in ref 36: 290.99 vs 290.93 eV. Our value is obtained by reevaluating the experimental spectrum presented in ref 34, which originally reported a significantly lower C2 vertical energy of 290.90 eV in good agreement with ref 36. Unfortunately, an error was made in ref 34 in the calculation of the vertical energy from the adiabatic energy. In the present work, the internal C1−C2 shift is determined to 2.57 eV when theoretical line-shape models are used, increasing to 2.59 eV when determined in a purely empirical fit to the observed spectrum. The theoretical shift is computed to 2.64 eV in the CCSD(T)/ECP approximation; cf. Table 3. Subtracting the difference between shifts obtained in ECP and explicit core hole calculations at the Hartree−Fock level of theory lowers our theoretical estimate of the C1−C2 shift to 2.59 eV, in agreement with our experimental result. This shift remains, however, 0.10 eV less than what is obtained from the C 1s energies reported in ref 36.

Chemical Shifts between Geometric Isomers. Carbon 1s spectra have been recorded for both *cis* and *trans* isomers of 1,2-dichloroethene and 1-chloropropene. The carbon atoms are equivalent in 1,2-dichloroethene, and as a result, there is only a single peak in the C 1s spectra to the right in Figure 1. It may be noted that our Franck−Condon model for *trans*-1,2-dichloroethene is clearly exaggerating the amount of vibrational excitation in this spectrum. The adiabatic C 1s ionization energies for the two isomers are equal to within half the experimental uncertainty, and although Table 3 reports an isomeric shift of 0.07 eV in the vertical ionization energy, this value is inflated by the problem with the Franck−Condon model. (For this reason, a larger uncertainty has been assigned to our reported vertical ionization energies for the *trans* isomer of 1,2-dichloroethene.)

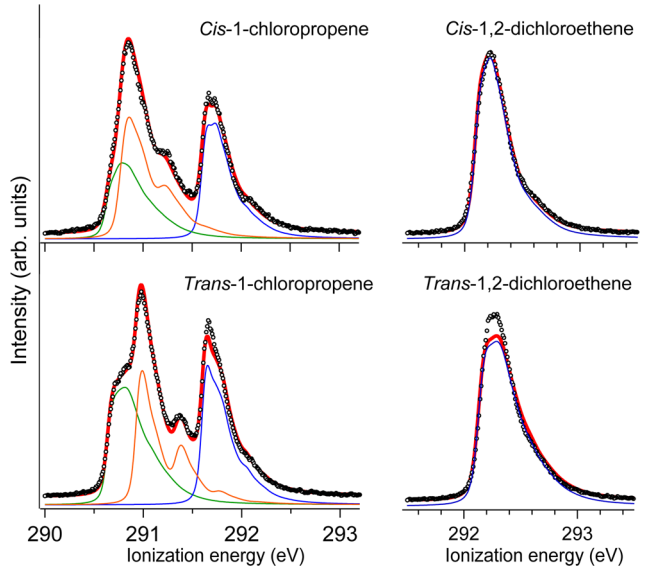


Figure 1. Carbon 1s photoelectron spectra of the *cis* and *trans* isomers of 1-chloropropene (left) and 1,2-dichloroethene (right). The spectra are fitted using one theoretical vibrational line shape for each chemically unique carbon: e.g., three different profiles for 1-chloropropene (in increasing ionization energy): C2 (=CH−, green), C3 ($-CH_3$, orange), and C1 (HClC=, blue).

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Figure 1 (left) shows the C 1s spectra of the two isomers of 1-chloropropene. Despite rather large differences in spectral appearance, the adiabatic ionization energies of the ethylene carbons are almost identical between the isomers. The methyl carbon, C3, on the contrary, shows a sizable isomeric shift of 0.17 eV. As the analysis of substituent effects (below) will be based on adiabatic energies for each of the ethylene carbons, 1-chloropropene will be represented by energies averaged over the two geometric isomers. This applies also to 1,2-dichloroethene.

Chemical Shifts between Rotamers. Both 3-chloropropene and 2,3-dichloropropene possess two stable rotational conformers, related through hindered rotation about the C2—C3 bond. This poses a number of issues in terms of modeling and interpretation of the corresponding C 1s spectra, including possible chemical shifts between the conformers, thermal excitation of the neutral molecule, and inadequacy of the harmonic vibrational model in the Franck−Condon analyses. To be specific, we consider 3-chloropropene, which exists as a *syn* conformer (Cl eclipsed by the C═C bond) and a *gauche* conformer (H eclipsed by the C═C) bond.

The relaxed torsional potential for the neutral 3-chloropropene molecule is included in the bottom of Figure 2 as computed at the B3LYP/tzp level of theory. Three minima are evident. Two of them, for the doubly degenerate *gauche* configuration, are equivalent. The unique minimum at zero dihedral angle corresponds to the *syn* configuration. The energy difference between the conformers is about equal to $2RT$, whereas the rotational barrier is twice as large. This implies that the torsional mode is thermally excited and that both conformations are populated at room temperature. Also included in the figure are rotational potentials for the three C 1s-ionized species. Ionization at C3 in the *syn* conformers evidently takes the molecule to a very shallow minimum and is likely to be accompanied by significant vibrational excitation. Moreover, there are noticeable shifts in the *gauche* equilibrium torsional angle for all three sites of ionization. In a previous section we outline briefly the construction of conformer-specific vibrational profiles that take into account the anharmonic nature of the torsional potentials and also thermal population of torsional states. (A detailed description of the procedure is given in the Supporting Information.)

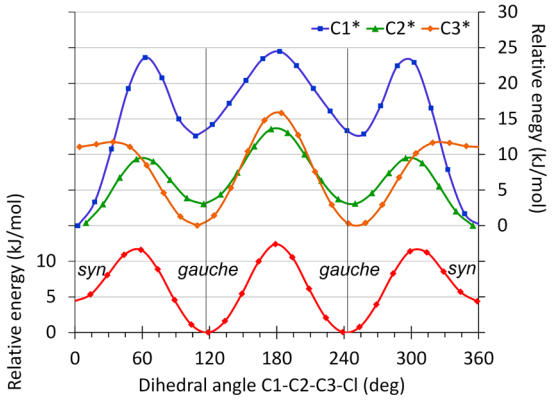


Figure 2. Torsional potential for the rotation of $-CH_2Cl$ in 3-chloropropene. The lower curve represents the ground-state potential (left axis), and the three ionized-state potentials are plotted against the right vertical axis. Each potential is plotted relative to its lowest energy and cannot be compared directly.

The C 1s photoelectron spectrum of 3-chloropropene as measured at room temperature is shown in Figure 3 (top). Also included in the figure are the conformer-specific vibrational line shapes fitted to the spectrum: *syn* (thin, dashed line) and *gauche* (thin, full line). The intensities are different for the two conformers, as expected from the energy difference evident in Figure 2. In the fit, the relative intensity between the two conformers was allowed to vary as one of the fitting parameters but was constrained to be the same for each site of ionization (e.g., for *syn* and *gauche*: $C1_{gauche}/C1_{syn} = C2_{gauche}/C2_{syn} = C3_{gauche}/C3_{syn}$). Although the accuracies of our computed rotational potentials are considered satisfactory for determining reliable vibrational line-shape models, the computed energy difference between the conformers is not sufficiently accurate to allow the evaluation of conformational populations. However, on the basis of the observed *syn*/*gauche* intensity ratio, one can compute the relative weights of the conformers.[37,38] For 3-chloropropene, we obtain a *syn* population of 18 ± 8%, in close agreement with the value of 18 ± 9% from gas electron diffraction data.[39]

Vibrational analyses of the C 1s spectra of 1,1-dichloropropene and 2,3-dichloropropene require a theoretical treatment similar to that just described, details of which are given as Supporting Information. For 2,3-dichloropropene, the energy difference between the *anti* conformer (characterized by a CCCCl dihedral angle of 0) and the doubly degenerate *gauche* conformer is small. From the relative intensities of the conformer-specific components indicated in Figure 3 (bottom) we find the *anti* population to be 52 ± 8%, in good agreement with 55 ± 8% at 24 °C, as obtained by Trongmo et al.[40] on the basis of gas electron diffraction data. In the case of 1,1-dichloropropene, the preferred rotamer changes from staggered orientation of the methyl group in the ground state, to an eclipsed geometry in the C2-ionized molecule.

Contrary to what was found for the geometric isomers of 1,2-dichloroethene and 1-chloropropene, the conformers of 3-chloropropene and 2,3-dichloropropene have significantly different adiabatic ionization energies for both C1 and C2.

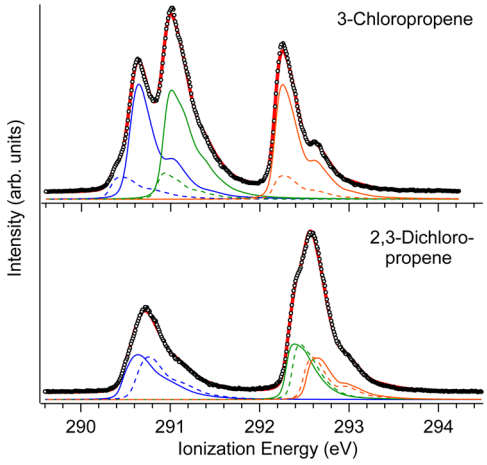


Figure 3. Carbon 1s photoelectron spectra of 3-chloropropene and 2,3-dichloropropene. The spectra were fitted using one theoretical profile for each chemically unique carbon [C1 (blue), C2 (green), and C3 (orange)] and for each conformer. Thus, six line shapes are needed to describe each spectrum. The less stable conformer is represented by dotted lines.

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Table 4. Substitution Parameters (eV) for X—HC_α=$C_\beta H_2$

	ΔIE[a]		ΔEKT[b]		ΔR[c]		Δq[d]	
carbon site:	α	β	α	β	α	β	α	β
Cl	1.51	0.05	1.92	0.48	0.41	0.43	0.27	0.04
CH_3	−0.08	−0.56	0.15	−0.28	0.23	0.28	0.14	−0.03
CH_2Cl, *gauche*	0.25	−0.20	0.66	0.35	0.41	0.55	0.17	0.01
CH_2Cl, *syn*	0.19	−0.34	0.61	0.10	0.42	0.44	0.11	0.03

[a]Standard errors 0.03 eV. [b]Calculated using MP4(SDQ)/(aug-)TZ. [c]ΔR = ΔEKT − ΔIE. [d]Mulliken atomic charge with H summed into C, from B3LYP/tzp.

Hence, the discussion of substituent effects will take into account conformational structure where appropriate.

Substituent Effects. The effect of replacing a hydrogen atom in ethene with a substituent (chlorine, methyl, or chloromethyl) is a change in C 1s ionization energy both at the site of substitution and at the neighboring sp^2 carbon. The observed shifts are used to define an ideal model void of direct or indirect interaction between substituents by assuming that effects from double (or higher) substitution may be obtained simply by adding shift parameters for each of the substituents as obtained in the single-substitution experiments. We are primarily concerned with chlorine as substituent, and when double or multiple substitution is considered, chlorine will always be one of the substituents. By contrasting the predictions from the additivity model with the chemical shifts that are actually observed, we are in position to identify and analyze nonadditivity effects, i.e., how the action of chlorine is modified by the presence of additional substituents.

Single Substitution on Ethene. By comparing experimental, adiabatic ionization energies for chloroethene to that of ethene, one finds that chlorine induces a large and positive shift of 1.51 eV in the C 1s energy of the carbon to which it is bonded (C1) and a much smaller, but still positive, shift of 0.05 eV in the ionization energy of the other carbon. To simplify the presentation, the sp^2 carbon atom to which a given substituent is bonded will be referred to as the α carbon, whereas the neighboring sp^2-hybridized atom is denoted by β. In this notation, chlorine gives rise to α and β shifts of 1.51 and 0.05 eV, respectively, as reported in the first row of Table 4. The corresponding α and β substituent shifts associated with methyl and chloromethyl are determined in a completely analogous manner from the C 1s energies of propene and 3-chloropropene; see Table 4.

The effect of a methyl substituent on ethene is quite different from that of a chloro substituent. First, the methyl substituent leads to lower C 1s ionization energies of both doubly bonded carbons, whereas a chloro substituent raises the ionization energy of both. Second, at the α carbon the effect of the methyl group on the ionization energy is small, whereas that for a chloro substituent is large. Third, at the β carbon the roles are reversed, with the methyl group causing a significant lowering of the ionization energy but the chloro substituent having almost no effect. (However, we will see below that the smallness of the effects noted here are the result of cancellation of significant, but opposite, effects of the substituents on the initial-state charge distribution and the final-state charge rearrangement.) The chloromethyl substituent comes intermediate between Cl and CH_3, affecting both carbon atoms in the double bond approximately equally strongly but in opposite directions. For the α carbon (C2 in 3-chloropropene), the ionization energy is increased by about 0.2 eV whereas at the β carbon there is a decrease in C 1s energy by 0.3 eV. It may also be noted that there is a considerable geometric effect from rotating the substituent from *gauche* to *syn* orientation, consistent with a through-space electrostatic effect from the negatively-charged chlorine atom in this substituent.

By means of electronic structure calculations, the observed substituent effects on C 1s ionization energies may be resolved into contributions from the charge distribution in the neutral ground-state molecule and the charge relaxation accompanying the ionization event. The initial-state contribution is computed according to the extended Koopmans theorem as outlined above (ΔEKT) whereas the relaxation term is obtained from the difference between the extended Koopmans theorem value and the experimental shift in ionization energy: ΔR = ΔEKT − ΔIE. These derived quantities are listed in Table 4.

The ΔEKT entries in Table 4 may loosely be thought of as changes in electrostatic potential induced by the various substituents at the indicated carbon atoms. These changes are brought about by the inductive and mesomeric effects of the substituents, which lead to modification of the charge on the carbon by charge transfer and to modification of the electric potential felt at the carbon because of the charge distribution in the rest of the molecule. The substituent ΔEKT values are in qualitative agreement with what may be anticipated from electronegativity: chlorine gives a strong positive shift at the α carbon of almost 2 eV, whereas chloromethyl induces a shift of about one-third of this, and methyl has only a small electrostatic effect on the atom to which it is bonded. For chlorine, the electrostatic effect is much reduced at the β carbon. This is the case but to lesser degree also for CH_2Cl, and the initial-state contribution is clearly responsible for the *gauche*−*syn* shift in C 1s energy as commented upon above for this substituent. There is a small positive effect of the methyl group at the α carbon, which is consistent with the higher electronegativity of the methyl group with respect to the hydrogen that it replaces. Most notable, however, is the negative electrostatic potential induced by the methyl substituent at the β site, consistent with charge transfer resulting from hyperconjugation (to be discussed below). This observation is supported by substituent-induced changes in Mulliken atomic charges, also included in Table 4.

Turning to final-state effects, the most striking observation is that the relaxations are very similar irrespective of whether ionization takes place at the substituted carbon or its neighbor, suggesting that the ethylene moiety acts as a unit as far as electronic relaxation upon charging is concerned. Moreover, the relaxation term shows rather less variation with substituent than does the companion initial-state component. In more detail, ΔR acts to cancel the electrostatic effects from chlorine on the β carbon, giving the appearance of very short reach for chlorine as a substituent. A similar cancellation is also at work for CH_3 at the α carbon, whereas relaxation reinforces the electrostatic contribution on the β carbon, effectively making methyl into a

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Table 5. Cl−X Substituent Interaction Parameters (eV)

	ΔIE[a]		ΔEKT[b]		ΔR[c]	
carbon site:	α	β	α	β	α	β
$\overset{Cl}{X}$>C_α=$C_\beta H_2$						
Cl—Cl	−0.20	−0.03	−0.26	−0.15	−0.07	−0.12
Cl—CH_3	−0.02	0.12	−0.02	0.02	0.00	−0.10
Cl—CH_2Cl, *gauche*	−0.06	0.05	−0.15	−0.08	−0.09	−0.13
Cl—CH_2Cl, *anti*	−0.07	0.07	−0.11	−0.08	−0.04	−0.15
Cl—C_αH=C_βH—X						
trans-Cl—Cl	−0.09		−0.12		−0.03	
cis-Cl—Cl	−0.10		−0.17		−0.07	
trans-Cl—CH_3	−0.03	0.00	−0.09	−0.09	−0.06	−0.09
cis-Cl—CH_3	−0.02	0.01	−0.02	−0.01	−0.01	−0.01
cis-Cl—CH_2Cl	−0.01	−0.01	−0.10	−0.08	−0.09	−0.07

[a]Standard errors 0.05 eV. [b]ΔEKT is calculated using MP4(SDQ)/(aug-)TZ. [c]ΔR = ΔEKT − ΔIE.

substituent that acts at a distance. The interplay between initial- and final-state effects makes chloromethyl appear as a meeker version of chlorine and methyl at the α and β carbons, respectively.

Double Substitution on Ethene: The Interplay between Chlorine and Cl, CH_3, and CH_2Cl. To first order and in the spirit of linear free-energy models, the impact on the C 1s energies of multiple substitutions in ethene may be estimated by adding substituent shifts as recorded in Table 4. For example, such a model would predict the ionization energies for C2 and C1 in *gauche*-2,3-dichloropropene to be 1.51 + 0.25 = 1.76 eV and 0.05 − 0.20 = −0.15 eV, respectively, to be compared to the observed shifts of +1.70 and −0.10 eV. In this particular case, the deviations of +0.06 eV (α) and −0.05 eV (β) between model and observations carry uncertainties of about 0.05 eV, i.e., similar in magnitude to the differences themselves. On the contrary, applying a similar analysis to *anti*-2,3-dichloropropene provides an independent evaluation of the same quantities. The two sets of deviations agree to within 0.02 eV, suggesting that the uncertainty of the departure from additivity is less than 0.05 eV. Hence, deviations larger than or equal to 0.05 eV will be taken as evidence for mutual interaction between the substituents. To explore this possibility, Table 5 lists substituent interaction parameters for doubly substituted ethenes having at least one chlorine substituent. These parameters are defined as the differences between the predictions of the additivity model and the experimentally observed C 1s ionization energies. Results are also given for the extended Koopmans energies and the relaxation energies.

From Table 5, the largest interaction term is found for dichloro substitution at the same carbon, with a departure from additivity of −0.20 eV in the ionization energy at the site of substitution (C_α). The second most important interaction is that between chlorine and methyl at the same carbon, which acts to increase the ionization energy at the unsubstituted sp^2 carbon (C_β) by 0.12 eV. There are also significant interaction terms between chlorine and chloromethyl when substituted at the same carbon. These terms are of similar magnitude and opposite sign at the two carbon sites and essentially insensitive to the orientation of the chloromethyl moiety.

To explore the origin of nonadditivity, the same kind of analysis is applied separately to the initial- and final-state contributions to the shifts in ionization energy; ΔEKT and Δ*R*, with the corresponding departures from additivity included in Table 5. The interaction between two chlorines is clearly dominated by initial-state effects, i.e., electrostatic interactions in terms of the ground-state electron density. In the dichloroethenes, the departure from additivity in C 1s energies is about −0.2 and 0.0 eV for C_1 and C_2, respectively, in the 1,1-substituted compound, leveling off to −0.1 eV in the 1,2-substituted isomers. A similar averaging in seen for the interaction between chlorine and chloromethyl, resulting in an apparent lack of interaction in *cis*-1,3-dichloropropene.

To explore the transferability of the chlorine−chlorine interaction energy, one may evaluate the corresponding quantity from ionization energies of the chlorinated methanes (with all chemical shifts evaluated relative to methane). From ref 30, the adiabatic ionization energy of chloromethane is 1.63(3) eV higher than that of methane, and within an additivity model one would thus expect the corresponding chemical shift of dichloromethane to be 2 × 1.63 eV.[41] The experimental value is 3.08 or 0.18 eV less than predicted from additivity, in good agreement with the Cl−Cl interaction term of −0.20 eV found in the present work. Moreover, from the corresponding initial-state energies,[42] the nonadditivity term in ΔEKT evaluates to −0.25 eV, again agreeing closely with present findings. It appears that the chlorine−chlorine interaction energy is similar in dichloromethane and 1,1-dichloroethene. Hence, we conclude that the chlorine−chlorine interaction is not much influenced by the π bond but is rather a consequence of competition for electrons through the C−Cl σ bonds.

The positive β interaction term between chlorine and methyl in 1-chloropropene evident in Table 5 derives largely from final-state relaxation. To explore this aspect further, we turn to quantifying the extent to which chlorine and methyl donate electrons to the β position via conjugation, before returning to their mutual interaction term.

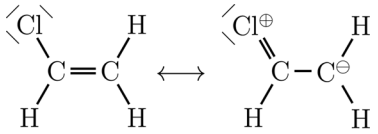
Π-Conjugation and Hyperconjugation. Weinhold and co-workers[43,44] have developed a set of tools for recasting the outcome of molecular orbital calculations into a language similar to that of valence bond theory. More specifically, a precomputed electron density is used to define atom-centered (core, lone-pair, and Rydberg) orbitals as well as 2-center bonding and antibonding orbitals. The resulting natural bonding orbitals (NBO) may be used as the basis to map a Lewis structure onto a single configurational wave function, and *vice versa*. Different from simple valence bond theory, however,

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

an NBO allows for unequal sharing of electrons between two atoms. This implies that bond polarity may be accounted for within a single Lewis structure, i.e., without invoking ionic resonance structures. After first identifying (in our case) a single reference Lewis structure that accounts for the largest fraction of the electron density, natural resonance theory (NRT) offers a systematic approach to identifying additional Lewis structures that are needed to describe the full electron density, and also for ranking these structures on a percentage scale according to how much they contribute to the electron density. These additional Lewis structures may be described by (integral) changes in bond orders or lone-pair occupancies relative to those present in the reference Lewis structure. In the present work, the occupancy of the antibonding counterpart to the π_{C1-C2} orbital turns out to be a particularly simple and useful measure of conjugative structures in the chlorinated ethenes and propenes.

To establish which resonance structures may be associated with the substituents of interest in this work, i.e., chlorine, methyl, and chloromethyl, we first consider chloroethene, propene, and 3-chloropropene, in their ground as well as the C 1s-ionized states with a core hole in the ethylene moiety. In these and all other molecules reported on in this study, the reference Lewis structure is the conventional one, featuring a carbon−carbon π bond.

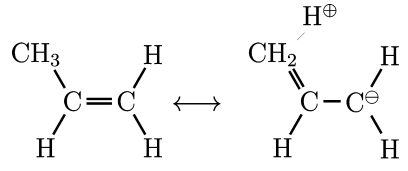
The two most important resonance structures for ground-state chloroethene are shown in the following scheme. The reference Lewis structure, I, is strongly dominating (weight 91.6%) whereas resonance structure II amounts to 4.6%.



I II

Structure II introduces electron delocalization by interaction between the π-bond and the Cl lone-pair of π-symmetry and is commonly described as π conjugation.[45] There are also additional, less important Lewis structures that will not be considered further. We find the same Lewis structures to apply to the C1 and C2 core-ionized states and the relative importance of the resonance structures in the C1-ionized state is quite similar to that of the ground state. This is in sharp contrast to the C2-ionized state, for which the weight of the regular, leading Lewis structure is only 83% and that of the π-conjugated structure becomes 13.7%. The importance of structure II is well reflected in the $\pi^*_{C_1C_2}$ occupancies, which are 0.08e, 0.09e, and 0.23e for the ground and two core-ionized states, respectively. Comparing initial and final states clearly shows that resonance structure II offers an efficient way of stabilizing the C2-ionized state by transferring electrons to the valence shell of C2. Presumably, the importance of structure II for the C2-ionized state derives from the Coulomb attraction between the positive charge on C2 and the electron transferred to this site. Though π conjugation is weaker in the initial and C1-ionized states than in the C2-ionized state and thus provides a relaxation mode that works to increase the internal C1−C2 shift in this molecule, relaxation by depolarizing the C−Cl σ bond is more important in the C1-ionized state due the proximity of Cl to C1. As mentioned above, this effect is included already in the definition of NBOs and does not show up as (σ) conjugation. Thus, in this molecule, the relaxation energies are large and similar for the two sites of core ionization, and the observed shift is essentially equal to the difference in initial-state potentials at the two sites.

Turning to propene, the neutral ground state is well represented by the conventional Lewis structure (weight 93.9%) augmented by two equivalent resonant structures (of combined weight of 2.1%). This particular resonance structure, II in the scheme below, is often described as hyperconjugation.[45] The two equivalent structures differ in which of the two out-of-plane C−H σ bonding orbitals is interacting with the $\pi^*_{C_1C_2}$ orbital.



I II

As discussed at some length in ref 46, the structural impact of hyperconjugation is in fact very small in propene, and even the rather low weight obtained in the natural resonance analysis may be exaggerated. However, it is important to note that even a small contribution from hyperconjugation can have a significant effect on the C 1s ionization energies and other properties. For instance, for propyne it has been noted that a transfer of −0.05e from the methyl group to the CH carbon can account for both the dipole moment and the shifts in ionization energy of both the CH_3 carbon and the CH carbon.[47] Turning to the C 1s-ionized states, the resonance picture of the C_2 core-ionized state is very similar to that of the ground state, and the same resonance structures are found also for the C_1-ionized state. However, in this latter case, the weight of the hyperconjugative structure is more than doubled, to 5.6%. In accordance with this, the occupancy of the $\pi^*_{C_1C_2}$ orbital is tripled from the ground state, from 0.033 to 0.099 electrons, as indicated in Table 6. This influence of hyperconjugation on C 1s ionization energies has been observed not only for propene[48,49] but also for 2-methylpropene,[48,49] propyne,[47] and 1,3-pentadiene.[33]

From the two first examples, we note that both methyl and chlorine facilitate electron transfer to the β site (the substituted carbon being the α site), by hyperconjugation and π conjugation, respectively. These resonance structures are greatly stabilized by core ionization at the β site and, using the change in π^* occupancy as measure of relaxation, chlorine, with a change of 0.15 electrons, is more than twice as effective as methyl (0.066) at a final-state stabilization of a core hole at the β carbon, as indicated by the entries in Table 6 for C2 of chloroethene, and C1 of propene.

3-Chloropropene is our example molecule to identify resonance structures associated with the chloromethyl substituent. These structures closely parallel those already accounted for in neutral and core-ionized propene, with the obvious replacement of chlorine for one of the methyl hydrogens. In the *gauche* conformer of this molecule, the chloromethyl substituent is oriented with one hydrogen in the plane of the ethylene moiety, which implies that one of the hyperconjugative structures features a chloronium rather than a proton. This leads to differences between the conformers but does not change the conclusion that chloromethyl and methyl are similar in terms of electron transfer by hyperconjugation, to C1 in the propene-based molecules.

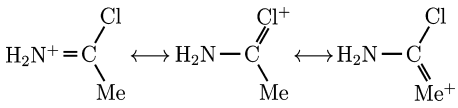
DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Table 6. Electron Occupancy of the $\pi^*_{C_1C_2}$ Orbital[a] from Natural Resonance Theory

compound	ground state	C_1-ionized state	C_2-ionized state
ethene	0.003	0.001	0.001
chloroethene	0.076	0.091	0.229
cis-1,2-dichloroethene	0.168	0.310	0.310
trans-1,2-dichloroethene	0.147	0.285	0.285
1,1-dichloroethene	0.152	0.156	0.396
trichloroethene	0.237	0.356	0.454
tetrachloroethene	0.316	0.509	0.509
propene	0.033	0.099	0.039
syn-3-chloropropene	0.033	0.097	0.044
gauche-3-chloropropene	0.029	0.125	0.040
2-chloropropene	0.102	0.273	0.112
anti-2,3-dichloropropene	0.097	0.264	0.110
gauche-2,3-dichloropropene	0.099	0.287	0.110
cis-1-chloropropene	0.104	0.169	0.236
trans-1-chloropropene	0.099	0.157	0.230
cis-1,3-dichloropropene	0.107	0.198	0.246
1,1-dichloropropene	0.169	0.215	0.382

[a]Calculated using B3LYP/tzp in state-optimized geometries.

The other molecules in this study are also analyzed by natural resonance theory; cf. Table 6 for a summary of occupation numbers of the $\pi^*_{C_1C_2}$ orbital. For the chlorinated ethenes, the increase in the π^* population due to C 1s ionization is closely represented by the following equation: $\Delta\pi^* = 0.008n_\alpha^{Cl} + 0.148n_\beta^{Cl} - 0.007n_\alpha^{Cl}(n_\alpha^{Cl} - 1) - 0.027n_\beta^{Cl}(n_\beta^{Cl} - 1) - 0.015n_\alpha^{Cl}n_\beta^{Cl}$. Here, n_α^{Cl} (n_β^{Cl}) is the number of chlorine substituents at (neighboring to) the ionized atom. The linear terms (0.015, 0.175) are close to those for chloroethene, whereas the additional terms show saturation effects that are an order of magnitude smaller than the linear β term. With only one propene derivative that is doubly chlorinated at the double bond, a similar analysis is not possible for the chlorinated propenes. Rather, we analyze the positive β interaction term in ΔIE between methyl and chlorine substituents (0.12 eV as reported in Table 5) by focusing on ionization at C1 in 2-chloropropene. Representing core-ionized carbon by its equivalent-cores counterpart, nitrogen, delocalization of the positive charge may be described by the following resonance structures:



Assuming additivity, electron transfer to π^* may be obtained by reference to the computed numbers for chloroethene (C2) and propene (C1) as provided in Table 6, which sums to an increase in π^* population of 0.22 electron. The same table lists the explicitly computed number for the C1-ionized state of 2-chloropropene as 0.273 − 0.102 = 0.17 electron. This indicates that the positive chlorine−methyl interaction may derive from slightly reduced electron donation because of interference in the core-ionized molecule between hyperconjugation (involving methyl) and π-conjugation (involving chlorine). This interference lowers the relaxation energy (and raises the ionization energy) from the value expected from additivity. This interpretation is supported by noting that the C−Cl bond contraction is larger for C2-ionized chloroethene than for C1-ionized 2-chloropropene, and similarly, the C2−C3 bond is more contracted following C1 ionization in propene than it is in 2-chloropropene. A similar picture is seen for the interaction between the two chlorines in 1,1-dichloroethene and between chlorine and the chloromethyl group in 2,3-dichloropropene. In each case the relaxation energy is about 0.1 eV lower than expected from additivity, and in each case the π^* population of the doubly substituted ethene is less than if predicted from additivity.

Comparison to Another Definition of Substituent Interaction Parameter. Exner and Böhm suggested[50] defining substituent interaction parameters through isodesmic reactions that bring two substituents into electronic contact with one another. More specifically, they quantified the interaction between substituents X and Y over an ethylene double bond by the heat of the metathesis reaction $H_2C{=}CHX + H_2C{=}CHY \rightarrow H_2C{=}CH_2 + XHC{=}CHY$. Different from the interaction parameters proposed in the preceding paragraph, which quantify the interaction of two substituents in terms of a local electronic effect, the Exner−Böhm approach is thermodynamic in its nature, quantifying the net molecular stabilization or destabilization arising from the interaction of two substituents. For this reason, we compare the sum of local (i.e., α and β) interaction parameters as proposed in the present work to Exner−Böhm interaction parameters. To illustrate, ref 50 lists a Cl−Cl interaction energy of 13.5 kJ mol^{-1}, which may be compared to twice the average of the *cis* and *trans* Cl−Cl interaction parameters listed in Table 5, amounting to −0.19 eV or −18.3 kJ mol^{-1}. One may extend this comparison to include also interaction between geminal substituents, i.e., to consider the heat of the reaction leading to 1,1- rather than 1,2-substitution: $H_2C{=}C{<}^{X}_{Y}$. This gives rise to Figure 4, which shows rather good (and negative) correlation between the two measures of substituent interaction.

Multiple Substitution on Ethene−1,1-Dichloropropene and Tri- and Tetrachloroethene. Three molecules in this study exemplify higher-than-double substitution of ethene and thus provide an opportunity to test the usefulness of pair-interaction terms in more complex molecules. To this end,

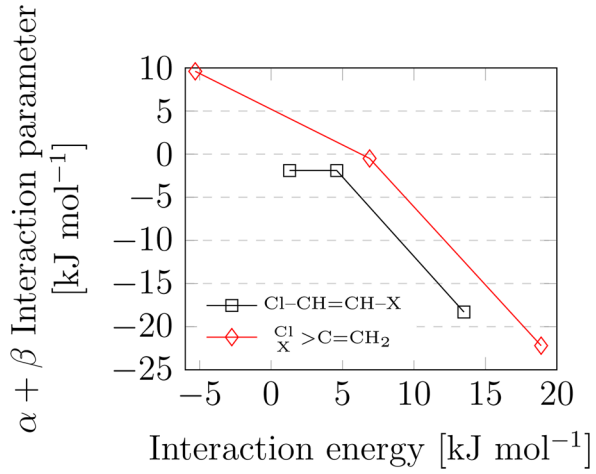


Figure 4. Sum of presently derived α and β substituent interaction parameters plotted against Exner−Böhm substituent interaction energies from electronic reaction energies as computed at the B3LYP/6-311+G(d,p) level of theory. All quantities gauge the interaction between chlorine and substituent X, for X = Cl, CH_2Cl, and CH_3; see main text for details.

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

Table 7. Departure from the Additivity Model (eV)

	ΔIE[a]		ΔEKT[b]	
carbon site →:	α	β	α	β
$Cl_2C_\alpha{=}C_\beta H_2$	−0.20	−0.03	−0.26	−0.15
$Cl_2C_\alpha{=}C_\beta HCH_3$	−0.19	0.03	−0.29	−0.15
$Cl_2C_\alpha{=}C_\beta HCl$	−0.34	−0.17	−0.47	−0.37
$Cl_2C{=}CCl_2$	−0.38		−0.73	

[a]Standard errors 0.05 eV. [b]Calculated using MP4(SDQ)/(aug-)TZ.

Table 7 summarizes the departure from additivity in experimental ionization energies and computed initial-state contributions in these molecules. From the vanishing 1,2-interaction term between methyl and chlorine one expects 1,1-dichloropropene to display similar departure from additivity as for 1,1-dichloroethene and this is borne out in the table.

The two molecules that display the largest departures from additivity in shifts in the C 1s ionization energies are tri- and tetrachloroethene. Working from the hypothesis that non-additivity effects may be resolved into a sum of interaction energies between pairs of substituents, one would expect a C1 ionization energy in trichloroethene, relative to that of ethene, of 2 × 1.51 + 0.05 + (−0.20) + (−0.09) + (−0.10) = 2.68 eV, using substituent and substituent interaction parameters from Tables 4 and 5, respectively. The resulting number agrees within experimental uncertainties with the observed value of 2.71 eV. Turning to tetrachloroethene, the simple additivity model predicts a shift in C 1s ionization energy of 2 × (1.51 + 0.05) = 3.12 eV, compared to the observed shift of 2.74(3) eV. There are six Cl−Cl pair interactions in this molecule, which add −0.20 + (−0.03) + 2 × (−0.09) + (−0.10) = −0.61 eV to take the estimated ΔIE from 3.12 to 2.51 eV. Thus, although inclusion of pairwise interaction terms significantly reduces the error inherent in the simple additivity model, clearly there are higher order interaction terms that gain importance with increasing degree of substitution. One contribution to this effect may be charge saturation, e.g., that carbon gets depleted of mobile electrons and hence the charge on each halogen atom gets less negative the more halogens there are, as documented for the halomethanes.[42,51]

CONCLUSIONS

High-resolution carbon 1s photoelectron spectra were recorded in the gas phase for six chlorosubstituted ethenes and seven chlorosubstituted propenes. By using theoretical Franck−Condon profiles in the analysis of these spectra, we obtained accurate and site-specific ionization energies for all of these molecules. For two molecules, 3-chloropropene and 2,3-dichloropropene, the analyses gave quantitative estimates of the relative populations of conformers in good accordance with previous estimates.

On the basis of core-level spectroscopy and models, chlorine, methyl, and chloromethyl are characterized in terms of their effect on the carbon 1s energy of the carbon to which they are attached (α site) as well as that of the neighboring sp^2 carbon (β site). The derived spectroscopic substituent parameters characterize both inductive effects and the ability of each substituent to engage in electron delocalization via the π system. Chlorine is characterized by a large, positive α parameter that reflects its ability to withdraw electrons from the atom to which it is attached. The corresponding β effect is small, however, due to cancellation between the electrostatic effect (which decreases with distance from the C−Cl bond dipole) and a rather substantial ability to donate electrons in both α and β positions. This is quite opposite to the substituent effect of methyl, which is an even mix of charge donation to the β site and acting as a polarizable unit.

By considering shifts in C 1s energies for doubly substituted ethenes, we extend the characterization of substituents to include also substituent−substituent interaction parameters. The accuracy of these parameters suffers from cumulative errors as they are obtained as higher order differences. One of the relatively large and clearly significant interaction parameters found is that between chlorine and methyl in the β-position to the site of interest, a case in question being C1 in 2-chloropropene. Analysis of the electronic structure of the core-ionized species by natural resonance theory indicates that the effect of two substituents on the relaxation energy is less than the sum of the effects of each substituent taken singly.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b05494.

Simplified molecular structures with labeling of carbon atoms, carbon 1s photoelectron spectra for all compounds studied (except for spectra included in the main text), theoretical shifts in C 1s energies for all the compounds studied as obtained using six different combinations of electronic-structure methods and basis sets, and detailed accounts of methods and procedures used to form Franck−Condon profiles, including torsional potentials for internal rotation about C−C bonds (PDF)

AUTHOR INFORMATION

Corresponding Author

*K. J. Børve. E-mail: Knut.Borve@uib.no.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge access to computer resources from the Norwegian high-performance computer consortium (NOTUR) through project number NN2506K. This work was also supported by the European Community Research Infrastructure Action under the FP6 Structuring the European Research Area Programme (through the Integrated Infrastructure Initiative Integrating Activity on Synchrotron and Free Electron Laser Science).

REFERENCES

(1) Hansch, C.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **1991**, *91*, 165−195.

(2) Kumar, K.; Carey, P. R. Resonance Raman Spectra and Structure of Some Complex Nitroaromatic Molecules. *J. Chem. Phys.* **1975**, *63*, 3697−3707.

(3) Lindberg, B.; Svensson, S.; Malmquist, P. Å; Basilier, E.; Gelius, U.; Siegbahn, K. Correlation of ESCA Shifts and Hammett Substituent Constants in Substituted Benzene Derivatives. *Chem. Phys. Lett.* **1976**, *40*, 175−179.

(4) Carroll, T. X.; Thomas, T. D.; Bergersen, H.; Børve, K. J.; Sæthre, L. J. Fluorine as a π Donor. Carbon 1s Photoelectron Spectroscopy

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

and Proton Affinities of Fluorobenzenes. *J. Org. Chem.* **2006**, *71*, 1961−1968.
(5) Takahata, Y. Substituent Effects in Chain and Ring Pi-Systems Studied by Core-Electron Binding Energies Calculated by Density Functional Theory. *Comput. Theor. Chem.* **2011**, *978*, 77−83.
(6) Sæthre, L. J.; Siggel, M. R. F.; Thomas, T. D. Effect of Halogen Substitutents on Carbon-1s Ionization Energies in Haloethenes and Haloethanes. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *49*, 119−137.
(7) Bässler, M.; Forsell, J.-O.; Björneholm, O.; Feifel, R.; Jurvansuu, M.; Aksela, S.; Sundin, S.; Sorensen, S. L.; Nyholm, R.; Ausmees, A.; et al. Soft X-Ray Undulator Beam Line I411 at MAX-II for Gases, Liquids and Solid Samples. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *101−103*, 953−957.
(8) Bässler, M.; Ausmees, A.; Jurvansuu, M.; Feifel, R.; Forsell, J.-O.; de Tarso Fonseca, P.; Kivimäki, A.; Sundin, S.; Sorensen, S. L.; Nyholm, R.; et al. Beam Line I411 at MAX II - Performance and First Results. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2001**, *469*, 382−393.
(9) Berrah, N.; Langer, B.; Wills, A. A.; Kukk, E.; Bozek, J. D.; Farhat, A.; Gorczyca, T. W. High-Resolution Angle-Resolved Measurements in Atoms and Molecules Using Advanced Photoelectron Spectroscopy at the ALS. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *101−103*, 1−11.
(10) Myrseth, V.; Bozek, J. D.; Kukk, E.; Sæthre, L. J.; Thomas, T. D. Adiabatic and Vertical Carbon 1s Ionization Energies in Representative Small Molecules. *J. Electron Spectrosc. Relat. Phenom.* **2002**, *122*, 57−63.
(11) Carroll, T. X.; Hahne, J. A.; Thomas, T. D.; Sæthre, L. J.; Berrah, N.; Bozek, J. D.; Kukk, E. Carbon 1s Core-Hole Lifetime in CO_2. *Phys. Rev. A: At., Mol., Opt. Phys.* **2000**, *61*, 042503.
(12) Dunning, T. H., Jr. Gaussian Basis Functions for Use in Molecular Calculations. III. Contraction of (10s6p) Atomic Basis Sets for the First Row Atoms. *J. Chem. Phys.* **1971**, *55*, 716−723.
(13) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650−654.
(14) McLean, A. D.; Chandler, G. S. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, Z = 11−18. *J. Chem. Phys.* **1980**, *72*, 5639−5648.
(15) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-Row Elements. *J. Chem. Phys.* **1982**, *77*, 3654−3665.
(16) Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-Consistent Molecular Orbital Methods 25. Supplementary Functions for Gaussian Basis Sets. *J. Chem. Phys.* **1984**, *80*, 3265−3269.
(17) Karlsen, T.; Børve, K. J.; Sæthre, L. J.; Wiesner, K.; Bässler, M.; Svensson, S. Toward the Spectrum of Free Polyethylene: Linear Alkanes Studied by Carbon 1s Photoelectron Spectroscopy and Theory. *J. Am. Chem. Soc.* **2002**, *124*, 7866−7873.
(18) Stevens, W. J.; Basch, H.; Krauss, M. Compact Effective Potentials and Efficient Shared-Exponent Basis Sets for the First- and Second-Row Atoms. *J. Chem. Phys.* **1984**, *81*, 6026−6033.
(19) Karlsen, T.; Børve, K. J. Accurate and Approximate Calculations of Franck-Condon Intensities in the Carbon 1s Photoelectron Spectrum of Methane. *J. Chem. Phys.* **2000**, *112*, 7979−7985.
(20) Pfaendtner, J.; Yu, X.; Broadbelt, L. J. The 1-D Hindered Rotor Approximation. *Theor. Chem. Acc.* **2007**, *118*, 881−898.
(21) Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(22) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. Gaussian Basis Sets for Use in Correlated Molecular Calculations. X. The Atoms Aluminum through Argon Revisited. *J. Chem. Phys.* **2001**, *114*, 9244−9253.
(23) Woon, D. E.; Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum through Argon. *J. Chem. Phys.* **1993**, *98*, 1358−1371.
(24) Peterson, K. A.; Dunning, T. H., Jr. Accurate Correlation Consistent Basis Sets for Molecular Core-valence Correlation Effects: The Second Row Atoms Al-Ar, and the First Row Atoms B-Ne Revisited. *J. Chem. Phys.* **2002**, *117*, 10548−10560.
(25) Børve, K. J.; Thomas, T. D. The Calculation of Initial-State Effects on Inner-Shell Ionization Energies. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *107*, 155−161.
(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision B.01; Gaussian Inc.: Wallingford, CT, 2009.
(27) Aidas, K.; Angeli, C.; Bak, K. L.; Bakken, V.; Bast, R.; Boman, L.; Christiansen, O.; Cimiraglia, R.; Coriani, S.; Dahle, P.; et al. The Dalton Quantum Chemistry Program System. *WIREs: Comput. Mol. Sci.* **2014**, *4*, 269−284.
(28) van der Straten, P.; Morgenstern, R.; Niehaus, A. Angular Dependent Post-Collision Interaction in Auger processes. *Z. Phys. D: At., Mol. Clusters* **1988**, *8*, 35−45.
(29) Carroll, T. X.; Berrah, N.; Bozek, J.; Hahne, J.; Kukk, E.; Sæthre, L. J.; Thomas, T. D. Carbon 1s Photoelectron Spectrum of Methane: Vibrational Excitation and Core-Hole Lifetime. *Phys. Rev. A: At., Mol., Opt. Phys.* **1999**, *59*, 3386−3393.
(30) Zahl, M. G.; Børve, K. J.; Sæthre, L. J. Carbon 1s Photoelectron Spectroscopy of the Chlorinated Methanes: Lifetimes and Accurate Vibrational Lineshape Models. *J. Electron Spectrosc. Relat. Phenom.* **2012**, *185*, 226−233.
(31) Kukk, E.; Snell, G.; Bozek, J.; Cheng, W.-T.; Berrah, N. Vibrational Structure and Partial Rates of Resonant Auger Decay of the N 1s→ 2π Core Excitations in Nitric Oxide. *Phys. Rev. A: At., Mol., Opt. Phys.* **2001**, *63*, 062702.
(32) Kukk, E.; Ueda, K.; Hergenhahn, U.; X, J. L.; Prümper, G.; Yoshida, H.; Tamenori, Y.; Makochekanwa, C.; Tanaka, T.; Kitajima, M.; et al. Violation of the Franck-Condon Principle Due to Recoil Effects in High Energy Molecular Core-Level Photoionization. *Phys. Rev. Lett.* **2005**, *95*, 133001.
(33) Thomas, T. D.; Sæthre, L. J.; Børve, K. J.; Gundersen, M.; Kukk, E. Reactivity and Core-Ionization Energies in Conjugated Dienes. Carbon 1s Photoelectron Spectroscopy of 1,3-Pentadiene. *J. Phys. Chem. A* **2005**, *109*, 5085−5092.
(34) Zahl, M. G.; Myrseth, V.; Andersen, T. H.; Harnes, J.; Borg, A.; Sæthre, L. J.; Børve, K. J. Molecular Spectra As a Tool in Assigning Carbon 1s Photoelectron Spectra of Physisorbed Overlayers. *J. Phys. Chem. C* **2010**, *114*, 15383−15393.
(35) Holme, A.; Børve, K. J.; Sæthre, L. J.; Thomas, T. D. Accuracy of Calculated Chemical Shifts in Carbon 1s Ionization Energies from Single-Reference *ab initio* Methods and Density Functional Theory. *J. Chem. Theory Comput.* **2011**, *7*, 4104−4114.
(36) Berndtsson, A.; Basilier, E.; Gelius, U.; Hedman, J.; Klasson, M.; Nilsson, R.; Nordling, C.; Svensson, S. Ethene and Chloroethenes Studied by ESCA. *Phys. Scr.* **1975**, *12*, 235−247.
(37) Thomas, T. D.; Sæthre, L. J.; Børve, K. J. Effects of Molecular Conformation on Inner-Shell Ionization Energies. *Phys. Chem. Chem. Phys.* **2007**, *9*, 719−724.
(38) Holme, A.; Børve, K. J.; Sæthre, L. J.; Thomas, T. D. Conformations and CH/π Interactions in Aliphatic Alkynes and Alkenes. *J. Phys. Chem. A* **2013**, *117*, 2007−2019.
(39) Schei, S. H.; Shen, Q. 3-Chloro-1-Propene (Allylchloride): Gas-Phase Molecular Structure and Conformations as Determined by Electron Diffraction. *J. Mol. Struct.* **1985**, *128*, 161−170.
(40) Trongmo, O.; Shen, Q.; Hagen, K.; Seip, R. Molecular Structure and Conformation of 2,3-Dichloro-1-Propene as Determined by Gas-Phase Electron Diffraction. *J. Mol. Struct.* **1981**, *71*, 185−194.
(41) Reference 42 reports a Cl−Cl interaction term of −0.13(1) eV. However, this value is obtained by fitting a quadratic model to a data set that includes tri- and tetrachloromethane. The quadratic term drops to −0.176 eV upon including cubic terms in the fitting model, in agreement with the presently reported value (−0.18 eV).
(42) Thomas, T. D.; Sæthre, L. J.; Børve, K. J.; Bozek, J. D.; Huttula, M.; Kukk, E. Carbon 1s Photoelectron Spectroscopy of Halomethanes. Effects of Electronegativity, Hardness, Charge Distribution, and Relaxation. *J. Phys. Chem. A* **2004**, *108*, 4983−4990.
(43) Weinhold, F.; Landis, C. R. *Discovering Chemistry with Natural Bond Orbitals*; John Wiley: Somerset, NJ, USA, 2012.

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493

(44) Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 6.0: Natural Bond Orbital Analysis Program. *J. Comput. Chem.* **2013**, *34*, 1429−1437 + 2134 (Erratum).
(45) Alabugin, I. V.; Gilmore, K. M.; Peterson, P. W. Hyperconjugation. *WIREs Comput. Mol. Sci.* **2011**, *1*, 109−141.
(46) Mo, Y.; Peyerimhoff, S. Theoretical Analysis of Electronic Delocalization. *J. Chem. Phys.* **1998**, *109*, 1687−1697.
(47) Sæthre, L. J.; Berrah, N.; Bozek, J. D.; Børve, K. J.; Carroll, T. X.; Kukk, E.; Gard, G. L.; Winter, R.; Thomas, T. D. Chemical Insights from High-Resolution X-Ray Photoelectron Spectroscopy and *ab initio* Theory: Propyne, Trifluoropropyne, and Ethynylsulfur Pentafluoride. *J. Am. Chem. Soc.* **2001**, *123*, 10729−10737.
(48) Sæthre, L. J.; Sværen, O.; Svensson, S.; Osborne, S.; Thomas, T. D.; Jauhiainen, J.; Aksela, S. High-Resolution C 1s Spectra of Methane, Ethene, Propene, and 2-Methylpropene. *Phys. Rev. A: At., Mol., Opt. Phys.* **1997**, *55*, 2748−2756.
(49) Sæthre, L. J.; Thomas, T. D.; Svensson, S. Markovnikov Addition to Alkenes. A Different View from Core-Electron Spectroscopy and Theory. *J. Chem. Soc., Perkin Trans. 2* **1997**, 749−755.
(50) Exner, O.; Böhm, S. Conjugation of Two Functional Groups through an Unsaturated System. *J. Phys. Org. Chem.* **2006**, *19*, 1−9.
(51) Wittmaack, B. K.; Crigger, C.; Guarino, M.; Donald, K. J. Charge Saturation and Neutral Substitutions in Halomethanes and Their Group 14 Analogues. *J. Phys. Chem. A* **2011**, *115*, 8743−8753.

DOI: 10.1021/acs.jpca.5b05494
J. Phys. Chem. A 2015, 119, 9481−9493