

Supplementary information for
Electronic Properties of Chlorine, Methyl, and
Chloromethyl as Substituents to the Ethylenic
Group
– Viewed from the Core of Carbon

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Table S1: Molecular Structures and Identification of Carbons C1, C2 and C3.

Etene derivative	C1 = C2	Propene derivative	C1 = C2 C3
Ethene	$\text{CH}_2 = \text{CH}_2$	Propene	$\text{CH}_2 = \text{CH} \begin{array}{l} \diagup \\ \text{CH}_3 \end{array}$
Chloroethene	$\begin{array}{l} \text{CH} = \text{CH}_2 \\ \diagup \\ \text{Cl} \end{array}$	<i>cis</i> -1-Chloropropene	$\begin{array}{l} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_3 \end{array}$
<i>cis</i> -1,2-Dichloroethene	$\begin{array}{l} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{Cl} \end{array}$	<i>trans</i> -1-Chloropropene	$\begin{array}{l} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_3 \end{array}$
<i>trans</i> -1,2-Dichloroethene	$\begin{array}{l} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{Cl} \end{array}$	2-Chloropropene	$\begin{array}{l} \text{CH}_2 = \text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_3 \end{array}$
1,1-Dichloroethene	$\text{CCl}_2 = \text{CH}_2$	3-Chloropropene	$\text{CH}_2 = \text{CH} \begin{array}{l} \diagup \\ \text{CH}_2\text{Cl} \end{array}$
Trichloroethene	$\text{CCl}_2 = \text{CH} \begin{array}{l} \diagdown \\ \text{Cl} \end{array}$	1,1-Dichloropropene	$\text{CCl}_2 = \text{CH} \begin{array}{l} \diagdown \\ \text{CH}_3 \end{array}$
Tetrachloroethene	$\text{CCl}_2 = \text{CCl}_2$	<i>cis</i> -1,3-Dichloropropene	$\begin{array}{l} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_2\text{Cl} \end{array}$
		2,3-Dichloropropene	$\begin{array}{l} \text{CH}_2 = \text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_2\text{Cl} \end{array}$

Table S2: Computed Shifts in Adiabatic Carbon 1s Ionization Energies (eV), Relative to that of Ethene.

Basis ^a		B3LYP	CCSD(T)		MP4(SDQ)		MP2
		<i>tzp</i>	<i>tzp</i>	(aug-)TZ	(aug-)TZ	(aug-)QZ	(aug-)QZ
Propene	C1	-0.660	-0.547	-0.572	-0.584	-0.590	-0.568
	C2	-0.096	-0.093	-0.083	-0.080	-0.073	-0.042
	C3	-0.031	-0.045	-0.061	-0.049	-0.048	-0.066
Chloroethene	C1	1.576	1.603	1.524	1.543	1.558	1.638
	C2	0.024	0.107	0.033	0.037	0.038	0.020
<i>cis</i> -1,2-Dichloroethene		1.496	1.593	1.458	1.480	1.496	1.548
<i>trans</i> -1,2-Dichloroethene		1.527	1.632	1.495	1.512	1.525	1.583
1,1-Dichloroethene	C1	2.973	3.010	2.881	2.915	2.941	3.097
	C2	0.056	0.189	0.054	0.058	0.059	0.033
Trichloroethene	C1	2.852	2.960	2.786	2.815	2.841	2.965
	C2	1.498	1.643	1.459	1.474	1.488	1.532
Tetrachloroethene		2.825	2.975	2.759	2.781	2.807	2.919
<i>cis</i> -1-Chloropropene	C1	0.940	1.065	0.970	0.974	0.983	1.080
	C2	-0.003	0.063	0.001	0.009	0.018	0.024
	C3	0.128	0.128	0.057	0.075	0.076	0.043
<i>trans</i> -1-Chloropropene	C1	0.934	1.062	0.970	0.980	0.990	1.087
	C2	-0.027	0.045	-0.004	0.009	0.019	0.027
	C3	0.271	0.281	0.230	0.251	0.254	0.226
2-Chloropropene	C1	-0.476	-0.335	-0.424	-0.432	-0.437	-0.422
	C2	1.498	1.500	1.448	1.469	1.489	1.587
	C3	0.399	0.399	0.324	0.340	0.340	0.324
3-Chloropropene, <i>gauche</i>	C1	-0.148	-0.049	-0.123	-0.128	-0.130	-0.102
	C2	0.343	0.346	0.294	0.296	0.302	0.344
	C3	1.603	1.606	1.520	1.545	1.564	1.595
3-Chloropropene, <i>syn</i>	C1	-0.340	-0.237	-0.319	-0.325	-0.331	-0.308
	C2	0.265	0.284	0.226	0.233	0.238	0.276
	C3	1.670	1.646	1.557	1.580	1.600	1.637
1,1-Dichloropropene	C1	2.352	2.486	2.347	2.363	2.381	2.552
	C2	0.056	0.154	0.054	0.060	0.068	0.062
	C3	0.301	0.325	0.229	0.248	0.248	0.207
<i>cis</i> -1,3-Dichloropropene	C1	1.391	1.497	1.360	1.375	1.389	1.487
	C2	0.366	0.420	0.305	0.315	0.326	0.335
	C3	1.680	1.707	1.578	1.615	1.634	1.642
2,3-Dichloropropene, <i>anti</i>	C1	-0.211	-0.076	-0.212	-0.215	-0.220	-0.208
	C2	1.782	1.799	1.692	1.716	1.733	1.835
	C3	2.016	2.010	1.872	1.900	1.919	1.955
2,3-Dichloropropene, <i>gauche</i>	C1	-0.050	0.075	-0.051	-0.055	-0.054	-0.035
	C2	1.837	1.837	1.737	1.756	1.776	1.883
	C3	1.929	1.943	1.814	1.846	1.865	1.896

^aComputational details may be found in the *Methods* section of the main paper.

Carbon 1s Photoionization Spectra

Carbon 1s photoionization spectra of both *cis* and *trans* isomers of 1-chloropropene and 1,2-dichloroethene are included as Fig. 1 in the main text, and similarly, the spectra of 3-chloropropene and 2,3-dichloropropene are included as Fig. 3. C1s spectra of the remaining 4 chloroethenes and 3 chloropropenes that are discussed in the paper are provided here as Figs. S1, S2, and S3. Some of the spectra that appear in the main text are repeated in the present figures in order to simplify the comparison of closely related spectra.

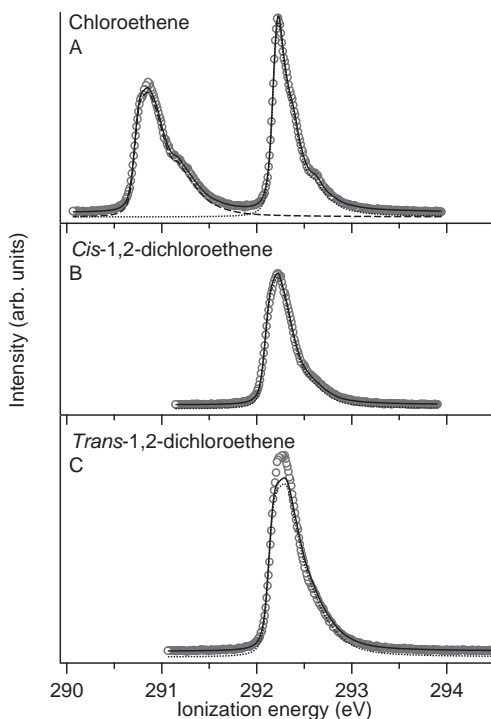


Figure S1: Carbon 1s photoelectron spectra of chloroethene, *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene. The overall fit (full line) to the experimental data (circles) is the sum of a constant background and one or two site-specific vibrational lineshapes, C1 (dotted) and C2 (dashed).

Computing Franck-Condon Profiles

This section first presents general aspects of how we compute Franck-Condon vibrational lineshape models for ionization events, covering cases where internal rotation either plays or

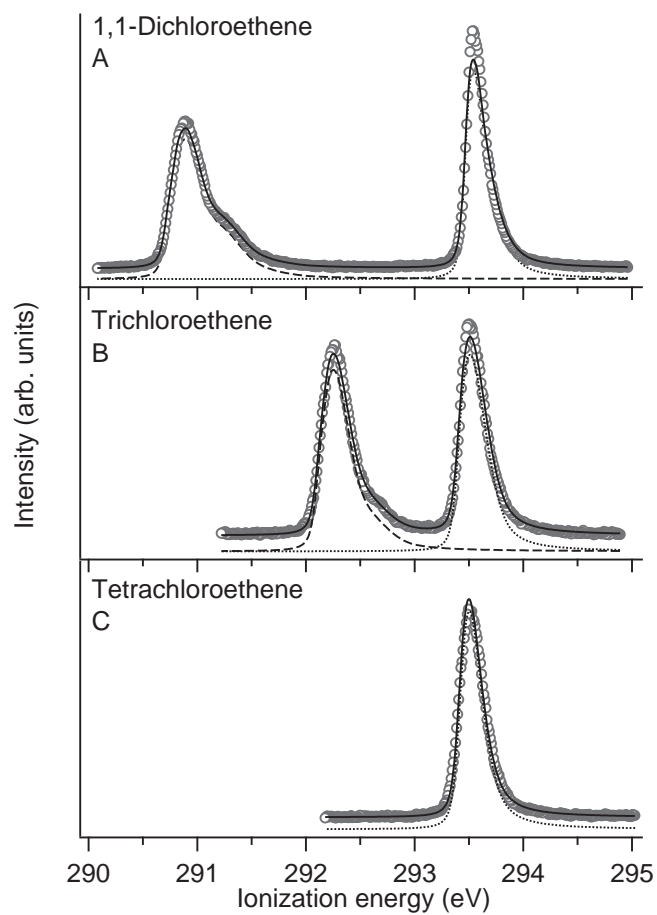


Figure S2: Carbon 1s photoelectron spectra of 1,1-dichloroethene, trichloroethene and tetrachloroethene. The spectrum of 1,1-dichloroethene was first published in Ref.¹ The overall fit (full line) to the experimental data (circles) is the sum of a constant background and one or two site-specific vibrational lineshapes, C1 (dotted) and C2 (dashed).

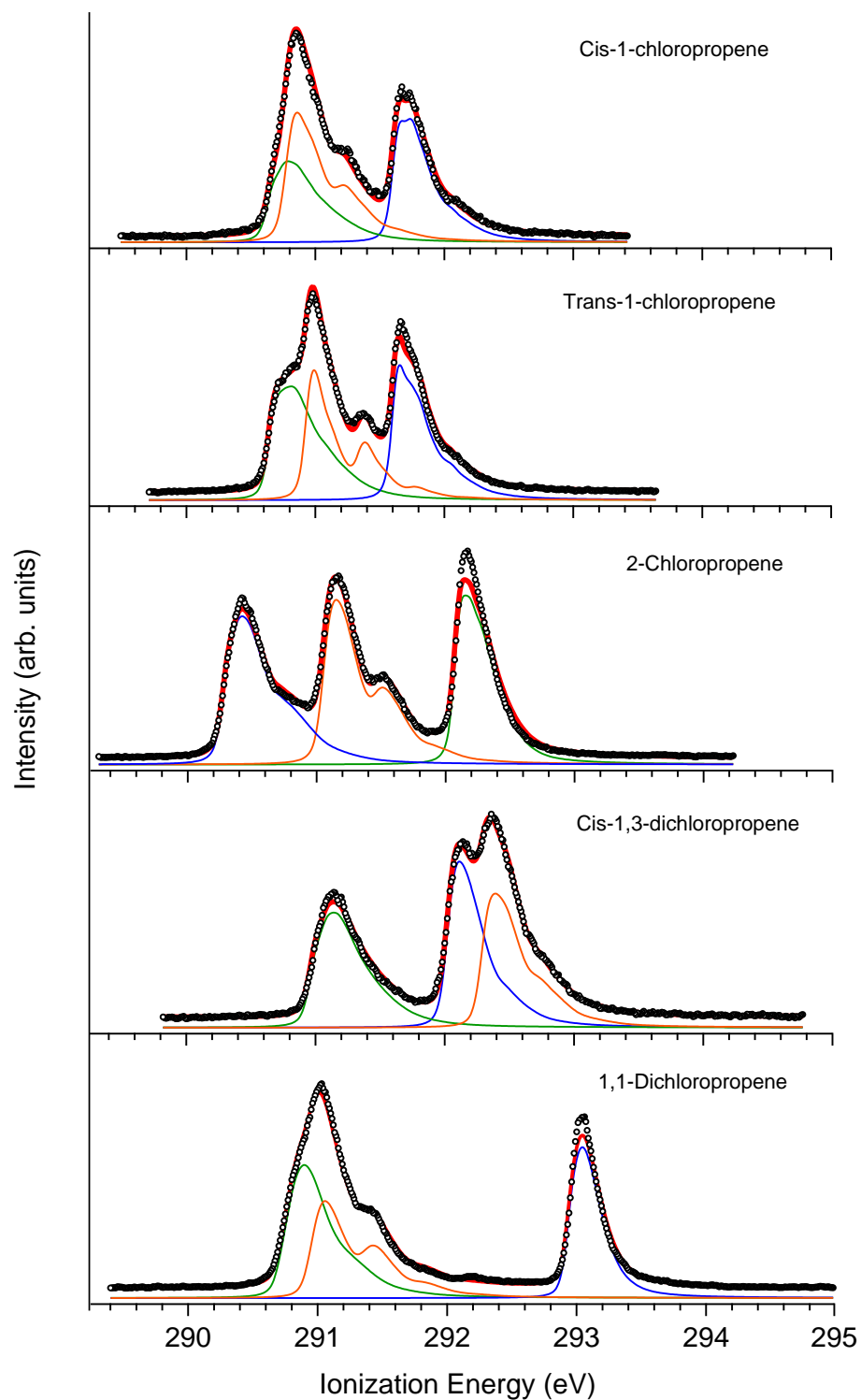


Figure S3: Carbon 1s photoelectron spectra of *cis*- and *trans*-1-chloropropene, 2-chloropropene, *cis*-1,3-dichloropropene and 1,1-dichloropropene. The overall fit (heavy red line) to the experimental data (circles) is the sum of three site-specific vibrational lineshapes, C1 (blue), C2 (green) and C3 (light red), and a constant background.

does not play a significant role. Next, potential curves for internal rotation are presented for relevant molecules included in this study. These potentials constitute a basis for deciding whether or not particular measures need to be taken to include anharmonic effects associated with internal rotation. The part of this section adds some comments on the two molecules for which internal rotation is a concern and which were not described in depth in the main text.

Approximations and Procedures

The geometries of the neutral and core-ionized species were first optimized using B3LYP/*tzp*, and harmonic vibrational frequencies and normal-mode vectors were computed at this level of theory. Information on the *tzp* basis set and the description of the ionized core may be found in the main text. To correct for anharmonicity and systematic errors, all frequencies were scaled by a factor of 0.99.² The frequency of the symmetric C*-H-stretching mode at the core-ionized carbon (C*) was scaled with an additional factor of 0.97 for sp² and 0.96 for sp³ hybridized carbons. The Franck-Condon analysis is particularly sensitive to changes in geometry following ionization and in order to increase the accuracy, all geometries were reoptimized using the CCSD(T) *ab initio* method with *tzp* bases. Additionally, to correct for the neglect of core-core and core-valence correlation as well as for basis-set deficiencies, the thus computed contraction of C*-H bonds was reduced by 0.2 and 0.3 pm for sp²- and sp³-hybridized carbons, respectively. Finally, normal modes and scaled frequencies obtained with B3LYP/*tzp* were combined with the changes in geometries computed at the higher level of electronic-structure theory.

After ensuring that initial- and final-state normal modes were paired off in an optimal manner, off-diagonal elements in the Duschinsky matrix were neglected during the evaluation of Franck-Condon (FC) integrals. The FC factors were computed in the harmonic approximation for all modes except where anharmonicity significantly affected either energies or intensities, or both, as detailed in the following. The symmetric C*-H stretching

mode was, whenever present, described by Morse potentials and the associated FC integrals were obtained by numerical integration.

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 presented below, the accompanying vibrational excitation was obtained in the 1-D hindered-rotor approximation.³ This implies that the torsional normal coordinate is approximated by an appropriate dihedral angle. In order to facilitate decoupling of the torsional mode from the other 3N-7 modes in the propenes, all normal modes and geometry changes were expressed in terms of internal (rather than Cartesian) coordinates.⁴ For the chlorinated ethenes, the projection of geometry changes onto normal modes were conducted in Cartesian coordinates.

The 1-dimensional Schrödinger equations for internal rotation were solved numerically for the neutral as well as the different core-ionized states followed by evaluation of Franck-Condon factors $|\langle \Psi_v | \Psi'_v \rangle|^2$ in terms of initial- and final-state torsional wave functions Ψ_v and Ψ'_v , respectively. The rotational potentials were obtained as relaxed scans in the appropriate dihedral angle; the moments of inertia of the internal rotors were obtained from the harmonic force constant and frequency in each case.⁵ There are typically a number of torsional states that are thermally populated in the neutral molecule. On the basis of the calculated wave functions, each initial wavefunction Ψ_v is classified in terms of the molecular conformer to which it primarily belongs – *gauche*, *anti*, *syn*, as appropriate.. For all of the thermally populated states we calculate FC factors for the ionization; there is one set of FC factors for each unique carbon. For each conformer and unique carbon we construct a Boltzmann-weighted profile. The Boltzmann factors are temperature dependent and are based on the theoretically calculated energies of the states relative to the lowest-energy state for that conformer. Finally, the conformer-specific torsional distributions are convoluted with Franck-Condon profiles for the 3N-7 other vibrational modes as obtained in the conventional manner (see above for details).

Torsional Potentials

The torsional potentials for rotation of the C3-group (CH_3 or CH_2Cl) in the ground states as well as C1 and C2 core-ionized states of selected chlorinated propenes are displayed in Figs. S4–S9. The corresponding potentials for rotation of $-\text{CClH}_2$ in 3-chloropropene were provided as Figure 2 in the main text and are not repeated here. The potentials were computed at the B3LYP/*tzp* level of theory using the ModRedundant function in Gaussian09. This option provides a relaxed scan of the potential energy surface, i.e., for fixed values of the dihedral angle describing the internal rotation, the energy is minimized by varying the remaining 3N-7 degrees of freedom. In the figures, each potential is plotted relative to its own minimum. In order to use these potential to define effective 1D hamiltonians for the torsional modes, one needs to obtain estimates of the effective moment of inertia.^{3,6} Useful accuracy was obtained by choosing the moment of inertia such that the harmonic frequency of the 1-dimensional model matches that of the corresponding mode in the full-dimensional system.⁶

Evaluation of the Importance of Internal Rotation

From Figs. S5–S8 we conclude that internal rotation does not provide a significant contribution to the Franck-Condon profiles for C1s ionization in either 1-chloropropene, 2-chloropropene or *cis*-1,3-dichloropropene, as these ionization processes are accompanied by only very minor changes in the relevant potential minima. This allows the harmonic model to be used for computing Franck-Condon factors based on the full potential energy surfaces (PES) for the ground- and ionized state. The assumption that the neutral molecule initially is in its vibrational ground state is also acceptable as far as the Franck-Condon profiles are concerned, although the methyl rotor is certainly thermally excited. This also applies to core-ionization at sites C1 and C3 in 1,1-dichloropropene, cf Fig. S4.

Different from the cases of C1 and C3, upon core-ionization of C2 in 1,1-dichloropropene, the potential surfaces of the ground and ionized states are quite different. As can be seen in

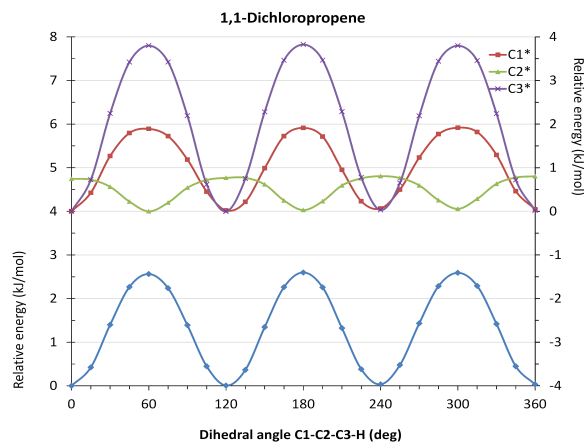


Figure S4: Potential curves for relaxed rotation of methyl in the ground state as well as the core-ionized states of 1,1-dichloropropene.

Fig. S4, a vertical transition from a ground-state minimum takes the system to a transition state on the final-state potential curve for rotation of the CH_3 -group. A purely harmonic model is clearly incapable of addressing this problem. Rather, the methyl rotation mode was decoupled from the remaining modes and treated as a 1-dimensional hindered rotor³ in the CCCH dihedral angle, giving rise to a single-mode Franck-Condon profile. The torsional mode has a low rotational barrier (200 cm^{-1}) and is therefore thermally excited in the ground state. This was taken into account by considering a Boltzmann distribution of vibrational initial states as described in the main text. The remaining $3N-7$ modes were described according to our standard procedure for preparing Franck-Condon (FC) profiles as outlined in the main text. Finally, the 1D rotational FC profile and the $3N-7$ vibrational profile were convoluted with each other to form the full model.

Based on the potential energy curves for torsion about the C2–C3 bond in 2,3-dichloropropene, it appears likely that this mode would be poorly described in the harmonic approximation, especially for C1-ionization of the *gauche* conformer. However, after forming FC profiles in the harmonic approximation as well as by using the 1D internal-rotor approach, it turns out that the differences between these models are negligible.

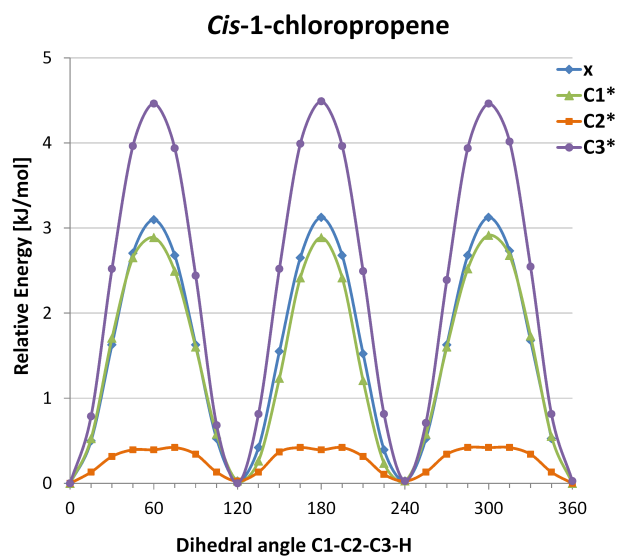


Figure S5: Torsional potentials for *cis*-1-chloropropene.

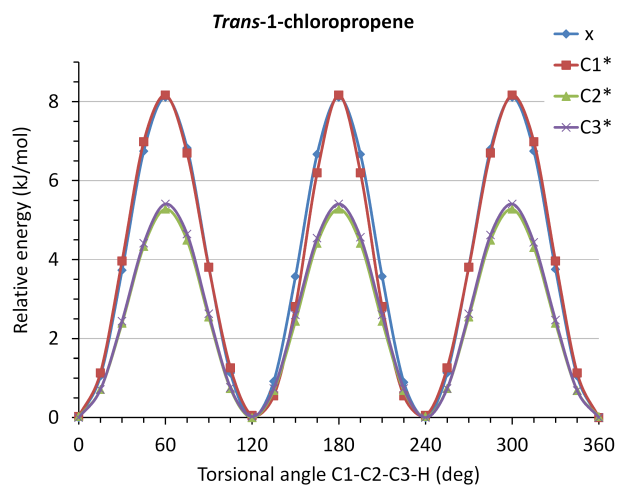


Figure S6: Torsional potentials for *trans*-1-chloropropene.

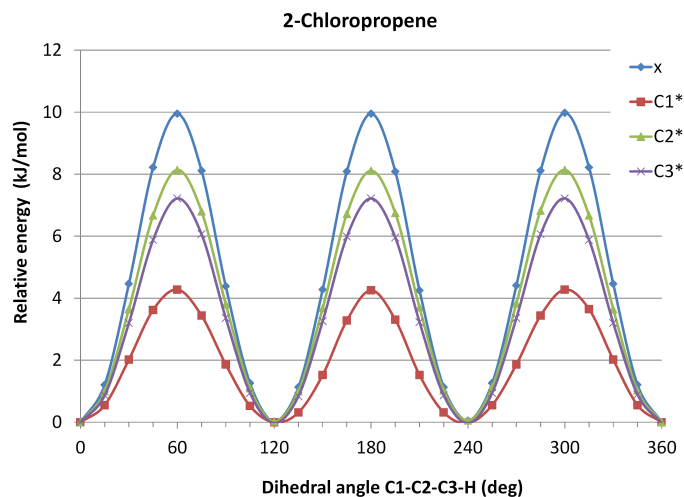


Figure S7: Torsional potentials for 2-chloropropene.

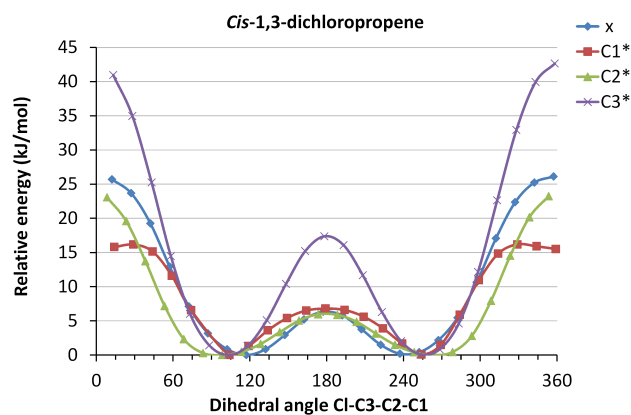


Figure S8: Torsional potentials for *cis*-1,3-dichloropropene.

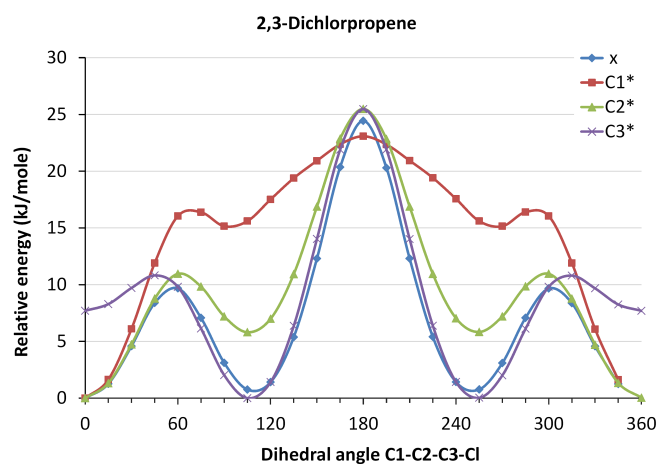


Figure S9: Potential curves for relaxed rotation of -CClH_2 in 2,3-dichloropropene.

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