

Ab Initio Highly Correlated Conformational Analysis of 1,2-Difluoroethane and 1,2-Dichloroethane

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Abstract: Temperature-dependent conformational population calculations for anti and gauche forms of 1,2-dichloroethane and 1,2-difluoroethane were carried out at a highly correlated level of theory (MP4(SDTQ) and CCSD(T)) employing good quality basis sets (6-311++G(3df,3pd) and aug-cc-pVQZ) for the determination of gas relative conformational energies, making use of the statistical thermodynamics formalism for the evaluation of the thermal energy correction at the MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ levels. In addition to the standard calculation of thermodynamic partition functions, a treatment of the lowest-frequency vibrational mode as hindered rotation and anharmonic correction to vibrational frequencies was also included. We found a good agreement between ab initio calculated conformational population values and experimental gas-phase electron diffraction data for the 1,2-dichloroethane. However, for the 1,2-difluoroethane species, a reasonable agreement with the experimental anti/gauche population ratio obtained from the analysis of gas-phase far-infrared (50–370 cm⁻¹) and low-frequency Raman (70–300 cm⁻¹) spectra was not obtained. The results reported here indicate that, for 1,2-difluoroethane, and probably other substituted alkanes where the gauche effect is of relevance, a more appropriated treatment of the low-frequency modes must be pursued in order to reproduce experimental conformational population data.

1. Introduction

Conformational analysis is a fascinating subject, first related to organic chemistry, which has attracted the attention of experimentalists and theoreticians for a long time, being also of great importance to almost all areas of chemistry. Over the past years, temperature-dependent nuclear magnetic

resonance (NMR) and solvent effect studies have been reported by many researchers in the area of organic chemistry; a recent example is the conformational analysis of succinic acid.¹ In several cases, the conformational process is not simple, with some vibrational modes being associated with small rotational barriers around C–C single bonds. Therefore, the rationalization of the governing factors operating on nonrigid molecules is still not completely clear, even for small systems, such as alkane-substituted molecules.² The substituted ethane molecules, such as 1,2-dichloroethane^{3–5} and 1,2-difluoroethane,^{3,6–8} have been the subject of a considerable number of investigations motivated by the interest in its restricted internal rotation.

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In addition, the recent literature for the simple nonsubstituted ethane molecule also shows that attention has been paid to the reason for the rotational barrier leading to the experimentally observed staggered structure.^{9,10} It is well-known that for 1,2-dichloroethane the anti form predominates over the gauche conformer. However, the opposite is observed for 1,2-difluoroethane, where both experimental and theoretical investigations have shown that this molecule prefers the gauche conformation, which has been successfully rationalized in terms of a hyperconjugation model.¹¹ So, in the case of the 1,2-difluoroethane molecule, the stability of the gauche conformation has been attributed to the high electronegative character of the fluorine atom denominated the *gauche effect*, where the equilibrium geometry is a result of charge transfer from the C–H electron to the C–F* antibonds.¹² Investigation of the far-infrared (50–370 cm⁻¹) and low-frequency Raman (70–300 cm⁻¹) spectra⁸ of the gas-phase sample of 1,2-difluoroethane showed that the gauche conformer is 3.39 ± 0.54 kJ mol⁻¹ more stable than the anti form, and it has been one of the most discussed cases of intramolecular interaction over the past three decades.

Analogously, the gauche preference of 1-fluoropropane¹² has also been recognized as of hyperconjugative nature. On the other side for butane,^{13,14} the anti preference has been attributed to steric hindrance or solvent effects. Freitas and Rittner² evaluated the conformational behavior of 1,2-disubstituted ethanes, where the bulky substituents are used, such as CN and NO₂ groups. They have shown that the electron delocalization contributes very differently to the conformational equilibrium of the 1,2-di-substituted ethanes. For example, for 1,2-dinitroethane, the contribution from electronic delocalization strongly favored the anti conformation, though antiperiplanar C–H/C–N(O₂) hyperconjugative, analogous to the interaction usually taken as the driving force of the gauche effect in fluorinated compounds, also showed a high energy. Although studies with model compounds search to describe the origin of the gauche effect, there is no general rule for this effect in the conformational isomerism of 1,2-di-substituted ethanes.^{2,15}

Concomitantly with the interest in the anti/gauche population ratio of substituted ethane, the ethane molecule^{9,16,17,4,10,11} has also been the subject of a considerable number of investigations addressing restricted internal rotation. The gas-phase spectroscopic and thermodynamic experimental data reported for ethane and ethane-substituted molecules provide useful information to assess the capability of available theoretical methods used to calculate temperature-dependent macroscopic properties. The theoretical determination of thermodynamic properties and, so, gas-phase conformational population (Gibbs population ratio) is based on the use of quantum mechanical methods and the standard statistical thermodynamics formalism,¹⁸ where thermodynamic quantities are calculated through the evaluation of electronic, translational, rotational, and vibrational molecular partition functions. The presence of low-frequency modes, which are not true vibrations, presents a challenge for the evaluation of the vibrational partition function that so far has no general solution, and therefore approximated treatments have been proposed. Various theoretical models have been developed

to account for the internal rotation problem. The most used recently reported treatments can be found, for example, in refs 19 and 20.

In order to investigate the performance of theoretical approaches for predicting relative gas-phase conformational population values, as compared to observed experimental data, two distinct points must be considered: the adequacy of the theoretical model employed, which is reflected in the pertinence of the mathematical equations developed, and the quality of the calculated energy values used to feed the mathematical functions to produce numerical values for the population ratio, which is dictated by the ab initio level of theory employed. Regarding the calculation of Gibbs conformational population we have, on one hand, the statistical thermodynamic formalism which makes use of molecular partition functions based on Boltzmann distributions and also additional corrections for hindered rotation through the use of empirical formulas, and on the other hand, the quantum mechanical methods available for the resolution of the time-independent Schrödinger equation for an isolated molecule in the vacuum, which produce the various energy values (electronic, rotational, and vibrational) and structural data to feed the thermodynamic partition functions. At this point, the validity of the theoretical approaches is attested to by comparison with experimental conformational population data within experimental uncertainties.

In the light of the importance of the gauche effect in conformational analysis studies, as mentioned in paragraphs before, we decided to investigate two experimentally well-known cases where, in one of them, this effect is of relevance: 1,2-dichloro- and 1,2-difluoroethane. Then, through comparison with available gas-phase experimental conformational population data, we aim to analyze the performance of the theoretical approaches commonly used to calculate conformational population values. In this work, we used the statistical thermodynamics formulas for the calculation of thermal energies employing ab initio post-Hartree–Fock (HF) quantum chemical methods to the calculation of geometrical parameters and harmonic frequencies required for the evaluation of rotational and vibrational partition functions.¹⁸ The theoretical model used in this article to describe the thermal energy corrections also included a hindered rotation treatment¹⁹ of low-frequency modes and anharmonicity correction^{21,22} to the vibrational frequencies for the evaluation of the vibrational partition function.

2. Computational Methodology

The equilibrium geometry of the two minimum-energy conformers (anti and gauche) found on the electronic ground-state potential energy surface (PES) for the 1,2-dichloroethane and 1,2-difluoroethane molecules were fully optimized with no symmetry constraint or other geometrical restriction at the second-order Møller–Plesset perturbation theory (MP2)²³ using Pople's split-valence 6-311++G(3df,3pd) basis set²⁴ and Dunning's correlated consistent basis set (aug-cc-pVTZ).²⁵ In addition, two first-order transition state (TS) structures connecting the anti and gauche conformers (named TS1) and two equivalent gauche forms (named TS2) were also located on the PES; therefore, energy barriers for

conformational interconversion could be calculated. The equilibrium structures (and TS) were fully optimized and vibrational frequencies, and therefore thermodynamic quantities, calculated at the MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ levels of theory. In order to obtain a better description of the electronic correlation effects, single-point energy calculations, using MP2 fully optimized geometries, were also carried out at the fourth-order Møller–Plesset perturbation theory with single, double, triple, and quadruple excitations (MP4(SDTQ))²⁶ and coupled cluster with single, double, and perturbative triple excitations (CCSD(T)).²⁷ For 1,2-difluoroethane, the G3(MP2) method²⁸ was also employed for the calculation of relative anti/gauche energies, in order to evaluate the gauche effect in the light of the G3(MP2) methodology as compared to the MP4(SDTQ) and CCSD(T) calculations.

The gas-phase thermal correction (ΔG_T) to the relative energy values ($\Delta E_{\text{ele-nuc}}$) was evaluated with the MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ structural parameters and harmonic vibrational frequencies and, then, used to obtain the gas-phase Gibbs free energy (ΔG) according to eq 1, where the double slash means that a MP4(SDTQ) or CCSD(T) single-point energy calculation was performed using the MP2 fully optimized geometry.

$$\Delta G = \Delta E_{\text{ele-nuc}}^{\text{MP4(SDTQ)//MP2,CCSD(T)//MP2}} + \Delta G_T^{\text{MP2}} \quad (1)$$

$\Delta E_{\text{ele-nuc}}$ in eq 1 represents the electronic plus nuclear repulsion energy contribution, originated from the resolution of the time-independent Schrödinger equation for an isolated molecule in the perfect vacuum, and the second term is the temperature-dependent thermal energy correction, which is given by eq 2:

$$\Delta G_T = \Delta U - T\Delta S \quad (2)$$

where ΔU is the internal energy correction to enthalpy which includes the zero-point energy (ZPE) contribution and $T\Delta S$ is the entropic contribution at the absolute temperature T . The mathematical expression for the terms on the right side of eq 2 and the respective definition of the electronic, translational, rotational, and vibrational partition functions can be found in ref 18. In analogy to eq 1, we can write the relative enthalpy as

$$\Delta H = \Delta E_{\text{ele-nuc}} + \Delta U \quad (3)$$

which gives directly $\Delta G = \Delta H - T\Delta S$, well-known from classical thermodynamics. The temperature range used was chosen according to the reported experimental data available (with $p = 1$ atm).

For the evaluation of the vibrational and rotational contributions to the thermal corrections given by eq 2, the harmonic oscillator (HO) and rigid rotor (RR) partition functions were used.¹⁸ The anharmonic correction was evaluated according to the procedure discussed in refs 21 and 22, using a second-order perturbative treatment based on quadratic, cubic, and semidiagonal quartic force constants, which consists of retaining the formal expression of the HO partition function, but the ZPE and vibrational frequencies (ν_i) are obtained at the anharmonic level. Therefore, in this approach, only the vibrational frequencies are corrected for

anharmonicity (the HO vibrational partition function was used). Explicit equations for anharmonic terms can be found in refs 21 and 22.

It has been well-known for well over half a century that a treatment of low-frequency vibrational modes, which are not true vibrations, as hindered rotations is required to describe the thermodynamics of ethane and ethane-substituted molecules. In ref 19, a treatment of low-frequency modes as internal hindered rotation is described in detail, with a procedure for the automatic identification of low-frequency modes as a hindered rotor, requiring no user intervention (implemented in the Gaussian computer code), being reported. Following early works of Pitzer and Gwinn²⁹ tabulating thermodynamic functions, formulas became available to interpolate the partition function between those of a free rotor, hindered rotor, and harmonic oscillators,^{29–32} with the approximation by Truhlar³¹ being used in many studies in recent years. In ref 19, a modified approximation to the hindered rotor partition function for the i th low-frequency mode (named here $q_i^{\text{Hind-Rot}}$) was given, which was used in this work. As stated in ref 19, this improved partition function keeps the good characteristics of the previous equation proposed by Pitzer and Gwinn,²⁹ while enhancing its behavior for low values of V_0/kT (V_0 is the barrier height for internal rotation, k the Boltzmann constant, and T the absolute temperature). These formulas (see ref 19) are for one normal vibrational mode involving a single rotating group with a clearly defined moment of inertia. The thermal corrections to enthalpy and Gibbs free energy, including hindered rotation and anharmonic correction to vibrational frequencies, are calculated according to eqs 4 and 5 below, at the MP2 level of theory and with good quality basis sets (6-311++G(3df,3pd) and aug-cc-pVTZ). The terms Hind-Rot and Anh indicate the use of hindered rotation and anharmonicity correction to vibrational frequency treatments, respectively, to account for deviations from the rigid rotor–harmonic oscillator (RR-HO) partition function.

$$\Delta U^{\text{Hind-Rot-Anh}} = \Delta U + \Delta U^{\text{Hind-Rot}} + \Delta U^{\text{Anh}} \quad (4)$$

$$\Delta G_T^{\text{Hind-Rot-Anh}} = \Delta G_T + \Delta G_T^{\text{Hind-Rot}} + \Delta G_T^{\text{Anh}} \quad (5)$$

All quantum chemical calculations were done with the Gaussian package,³³ where the hindered rotation treatment and anharmonicity correction calculations are readily implemented, at the Laboratório de Química Computacional e Modelagem Molecular, Departamento de Química, Universidade Federal de Minas Gerais, and also Núcleo de Estudos em Química Computacional, Departamento de Química, Universidade Federal de Juiz de Fora.

3. Results and Discussions

Table 1 reports the calculation of absolute entropy for ethane at room temperature, using the MP2 level of theory and a series of Pople's split-valence basis sets, with the aid of the standard statistical thermodynamics formalism with the inclusion of a treatment of the hindered-rotation effects and anharmonicity correction to vibrational frequencies, as explained in the methodology section. These data are shown only for reasons of comparison, since a number of theoretical

Table 1. MP2 Calculation of Absolute Entropy ($\text{J mol}^{-1} \text{K}^{-1}$) of the Ethane Molecule in the Staggered Form ($T = 298 \text{ K}$, $p = 1 \text{ atm}$) Employing Diverse Basis Sets

Entropy	6-31G (d,p)	6-311++G (d,p)	6-311++G (2d,2p)	6-311++G (2df,2pd)	6-311++G (3df,3pd)	aug-cc-pVTZ
S^a	226.65	227.11	227.27	227.23	227.15	227.32
$S^{\text{True-Vib } b}$	221.50	221.79	221.67	221.75	221.71	221.75
$S^{\text{Hind-Rot-Anh } c}$	228.07	228.74	228.91	228.86	228.86 {0.3%} ^d	229.03 {0.2%} ^d

^a Absolute entropy calculated using the standard statistical thermodynamics partition function (particle in a box; rigid rotor and harmonic oscillator approximations for translational, rotational, and vibrational contributions) including all 3N-6 vibrational modes as harmonic oscillators. $S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}}$ ($S_{\text{trans}} = 151.17$ and $S_{\text{rot}} = 68.03 \text{ J mol}^{-1} \text{K}^{-1}$ (MP2/6-311++G(3df,3pd) value). $1 \text{ cal} = 4.184 \text{ J}$. ^b The low-frequency mode was excluded from the evaluation of the vibrational partition function for the calculation of the absolute entropy, so 3N-7 normal modes were used. Only the true vibrational modes that can be satisfactorily described as harmonic oscillators were considered. The low-frequency contribution to entropy ($S_{\text{vib}}^{\text{Low-Freq}}$) is $5.44 \text{ J mol}^{-1} \text{K}^{-1}$. $S_{\text{vib}}^{\text{True-Vib}} = 2.51 \text{ J mol}^{-1} \text{K}^{-1}$; $S_{\text{vib}}^{\text{Low-Freq}} = 5.44 \text{ J mol}^{-1} \text{K}^{-1}$; $S_{\text{vib}}^{\text{Hind-Rot}} = 1.05 \text{ J mol}^{-1} \text{K}^{-1}$; $S_{\text{vib}}^{\text{Anh}} = 0.67 \text{ J mol}^{-1} \text{K}^{-1}$. $S_{\text{vib}}^{\text{Hind-Rot-Anh}} = S_{\text{vib}}^{\text{True-Vib}} + S_{\text{vib}}^{\text{Low-Freq}} + S_{\text{vib}}^{\text{Hind-Rot}} + S_{\text{vib}}^{\text{Anh}} = 9.67 \text{ J mol}^{-1} \text{K}^{-1}$. ^c Absolute entropy value calculated with the inclusion of anharmonicity and hindered internal rotation corrections for the evaluation of the vibrational partition function. ^d Percent error relative to the experimental entropy value ($229.49 \pm 0.8 \text{ J mol}^{-1} \text{K}^{-1}$) obtained at 298.1 K from ref 35. The corresponding errors for the TS value are only 0.17 and 0.13 kJ mol^{-1} , respectively, for the 6-311++G(3df,3pd) and aug-cc-pVTZ basis sets.

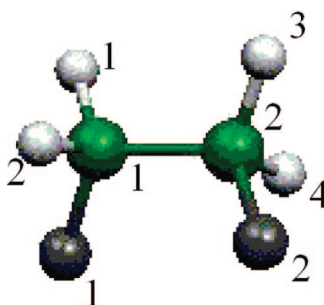
studies have been reported for the simple ethane molecule. When the values given in the last column of Table 1 are analyzed, it can be seen that the entropy calculated with the aug-cc-pVTZ basis set deviates only $0.17 \text{ J mol}^{-1} \text{K}^{-1}$ from the value calculated with Pople's split valence basis set, with a smaller deviation obtained when the low-frequency mode is ignored ($0.04 \text{ J mol}^{-1} \text{K}^{-1}$). From the results reported in Table 1, it can be seen that the combination of anharmonic correction to vibrational frequencies and a hindered rotor treatment of the lowest-frequency modes provides a perfect description of the entropy of ethane at room temperature, when a large basis set is used (at least 6-311++G(2d,2p)) with a MP2 calculation. The deviation from the experimental value is only 0.3% (0.2% with the aug-cc-pVTZ basis set), which is within the experimental uncertainty of $\pm 0.63 \text{ J mol}^{-1} \text{K}^{-1}$. Therefore, for the ethane molecule, the approach used worked very well, an expected and well-known result in the literature. It is worth mentioning that the MP2/6-311++G(3df,3pd) total entropy (the sum of electronic, translational, rotational, and vibrational contributions is $228.86 \text{ J mol}^{-1} \text{K}^{-1}$) has a relatively small vibrational contribution of $9.67 \text{ J mol}^{-1} \text{K}^{-1}$, which, however, is assumed to play the key role when comparison with experimental data is made. The potential barrier for ethane ($V = \frac{1}{2}V_0(1 + \cos 3\varphi)$) was also calculated at the MP2, MP4(SDQ), MP4(SDTQ), CCSD, and CCSD(T) levels of theory (MP2-optimized geometries), with the 6-311++G(3df,3pd), aug-cc-pVTZ, and aug-cc-pVQZ basis sets (*staggered* \rightarrow *eclipsed* process). We found a smooth dependence with the level of electron correlation for all methods showing a very reasonable agreement with experimental results within experimental uncertainties (the CCSD(T)/6-311++G(3df,3pd)/MP2/6-311++G(3df,3pd) value is $11.80 \text{ kJ mol}^{-1}$ and the experimental value $12.03 \pm 0.52 \text{ kJ mol}^{-1}$).

An assessment of the suitability of the MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ levels of calculation to evaluate geometrical parameters, rotational constants, and vibrational frequencies, required by the numerical calculation of partition functions, can be made by analyzing the data reported in Tables 2 and 3 for 1,2-difluorethane (as an example). The good agreement with experimental results shown in Table 2 for the rotational constants guarantees that the rotational partition function is satisfactorily well-represented at the MP2 level of theory. The same holds for

the comparison between experimental and theoretical vibrational frequencies reported in Table 3. When anharmonicity correction is included, the deviation between experimental gas-phase vibrational frequencies and calculated anharmonic frequencies is below 50 cm^{-1} for the CH stretch vibrations (high frequencies), being even smaller for deformation and twist modes (less than 20 cm^{-1}) and lower frequency modes below 1000 cm^{-1} (less than 5 cm^{-1}).

Figure 1 shows calculated MP2 thermal quantities (ΔU and ΔG_T) using various basis sets for the anti \rightarrow gauche process for 1,2-difluorethane (a similar behavior was found for 1,2-dichloroethane). It can be seen from Figure 1 that the thermal corrections reached nearly unchanged values within $\pm 0.08 \text{ kJ mol}^{-1}$ at the MP2/6-311++G(3df,3pd) level of theory for geometry optimization and harmonic frequency calculation (the same conclusion is reached with the aug-cc-pVTZ basis set), a variation that would cause a change on the calculated conformational population of less than 1% . It is worth saying that an MP4 or CC geometry optimization and frequency calculation with a triple- ζ -quality basis set for 1,2-difluorethane and 1,2-dichloroethane is unthinkable; even so, we would not expect a significant modification of the pattern exhibited in Figure 1. Just recently, we have performed MP4(SDQ) and CCSD geometry optimizations and harmonic frequency calculations, employing the 6-311++G(2d,2p) and aug-cc-pVDZ basis sets, for the CF_2Cl_2 species,³⁷ with the results being in excellent agreement with MP2 calculations, which adds confidence to our expectation regarding the trend shown in Figure 1.

The effect of the electronic correlation and size of the basis set on relative electronic plus nuclear repulsion energies ($\Delta E_{\text{ele-nuc}}$) can be analyzed from the results reported in Figure 2 for 1,2-difluorethane (a similar pattern was obtained for 1,2-dichloroethane). It can be seen that the MP4(SDTQ) and CCSD(T) relative energies for the anti \rightarrow gauche process agree within less than 0.21 kJ mol^{-1} , showing a welcome smooth behavior of the energy values as a function of the level of theory and basis set quality. It can also be seen from Figure 2 that the difference between the CCSD(T)/6-311++G(3df,3pd) and CCSD(T)/aug-cc-pVQZ relative energies is less than 0.08 kJ mol^{-1} , so the use of MP2/6-311++G(3df,3pd) thermal corrections and CCSD(T)/6-311++G(3df,3pd) relative energies can be justified. We may

Table 2. *Ab Initio* and Experimental Geometrical Parameters (the Atomic Labels Are Defined Below) and Rotational Constants for the 1,2-Difluoroethane gauche Conformer^a

	exptl.	6-31G(d)	6-311++G(2d,2p)	6-311++G(3df,3pd)	aug-cc-pVDZ	aug-cc-pVTZ
Bond Distances (Å) ^b						
C ₁ –C ₂	1.493 ± 0.002	1.501	1.498	1.499	1.507	1.499
C ₁ –F ₁ (=C ₂ –F ₂)	1.390 ± 0.003	1.392	1.392	1.383	1.407	1.388
C ₁ –H ₁ (=C ₂ –H ₃)	1.099 ± 0.002	1.095	1.088	1.090	1.102	1.091
C ₁ –H ₂ (=C ₂ –H ₄)	1.093 ± 0.004	1.093	1.086	1.088	1.100	1.089
Bond Angles (deg) ^b						
F ₁ –C ₁ –C ₂ (=F ₂ –C ₂ –C ₁)	110.6 ± 0.5	109.5	110.0	110.3	110.3	110.3
H ₁ –C ₁ –C ₂ (=H ₃ –C ₂ –C ₁)	108.4 ± 0.6	110.3	110.7	110.6	109.7	110.7
H ₂ –C ₁ –C ₂ (=H ₄ –C ₂ –C ₁)	113.3 ± 0.6	110.3	109.9	109.7	111.0	109.7
F ₁ –C ₁ –H ₁ (=F ₂ –C ₂ –H ₃)	109.6 ± 0.3	108.6	108.0	108.1	107.8	108.0
F ₁ –C ₁ –H ₂ (=F ₂ –C ₂ –H ₄)	107.8 ± 0.6	108.5	108.1	108.2	107.7	108.2
H ₁ –C ₁ –H ₂ (=H ₃ –C ₂ –H ₄)	109.1 ± 0.5	109.6	110.1	109.9	110.3	110.0
Torsion Angle (deg) ^b						
F–C–C–F	71.0 ± 0.3	68.9	70.5	70.3	70.7	70.8
Rotational Constants (MHz) ^b						
A	17322	16855 ^c	17158	17349	16871	17295
B	5013	51448 ^c	5062	5073	4954	5040
C	4383	44505 ^c	4409	4424	4318	4400

^a Theoretical values were obtained using the MP2 level and employing various basis sets. ^b Microwave values taken from ref 36. Symmetry number: $\sigma = 2$. ^c The corresponding MP2/6-311G(d,p) A, B, and C values are respectively 17234, 5060, and 4410 MHz.

Table 3. Experimental and *ab Initio* MP2 Vibrational Frequencies for the 1,2-Difluoroethane Gauche Conformer

vibrational frequencies (cm ⁻¹) ^a	exptl.	MP2/6-311++G (2d,2p)		MP2/6-311++G (3df,3pd)	MP2/aug-cc-pVDZ	MP2/aug-cc-pVTZ
	observed frequencies	anharmonic frequencies ^b	harmonic oscillator	harmonic oscillator	harmonic oscillator	harmonic oscillator
FCCF torsion	147	151	153	154	151	154
CCF bend	327	326	326	328	319	326
CCF bend	500	498	501	506	491	502
CC stretch	865	868	885	892	874	886
CH ₂ rock	896	895	914	920	893	915
CF stretch	1076	1066	1090	1109	1071	1101
CF stretch	1079	1095	1122	1142	1110	1135
CH ₂ rock	1116	1123	1148	1150	1139	1146
CH ₂ twist	1244	1251	1278	1278	1250	1274
CH ₂ twist	1284	1296	1322	1323	1296	1318
CH ₂ wag	1377	1393	1427	1418	1388	1415
CH ₂ wag	1410	1425	1462	1457	1435	1453
CH ₂ deformation	1460	1476	1516	1513	1480	1513
CH ₂ deformation	1460	1478	1517	1513	1484	1513
CH ₂ symmetric stretch	2958	2997	3105	3094	3094	3091
CH ₂ symmetric stretch	2985	3004	3114	3101	3102	3098
CH ₂ antisymmetric stretch	2995	3030	3173	3163	3169	3158
CH ₂ antisymmetric stretch	3001	3042	3185	3174	3179	3169

^a Experimental values and assignments obtained from a gas-phase infrared and Raman study reported in ref 8. ^b Evaluated including anharmonic corrections.

say that the MP4(SDTQ) and CCSD(T) conformational energies might be trusted with a rough uncertainty estimated at ± 0.21 kJ mol⁻¹, based on the pattern shown in Figure 2, with a corresponding uncertainty in the conformational population of approximately 1%. Nevertheless, as will be

shown later, this 1% of uncertainty cannot be blamed when a comparison with experimental results is made. The reported uncertainties for experimental conformational populations are in the range of ± 2 –5%, and the uncertainty value for experimental enthalpy determination is within ± 0.4 –0.8 kJ

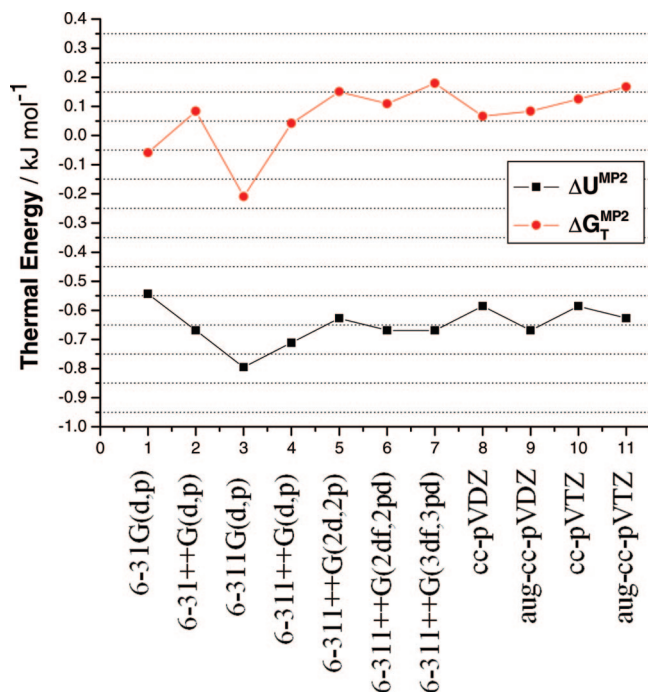


Figure 1. Anti \rightarrow gauche MP2 thermal energy (at room temperature) variation for 1,2-difluoroethane as a function of the basis set quality. The MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ $T\Delta S$ (entropic contribution) values are respectively -0.84 and -0.80 kJ mol^{-1} ($\Delta G_T = \Delta U - T\Delta S$).

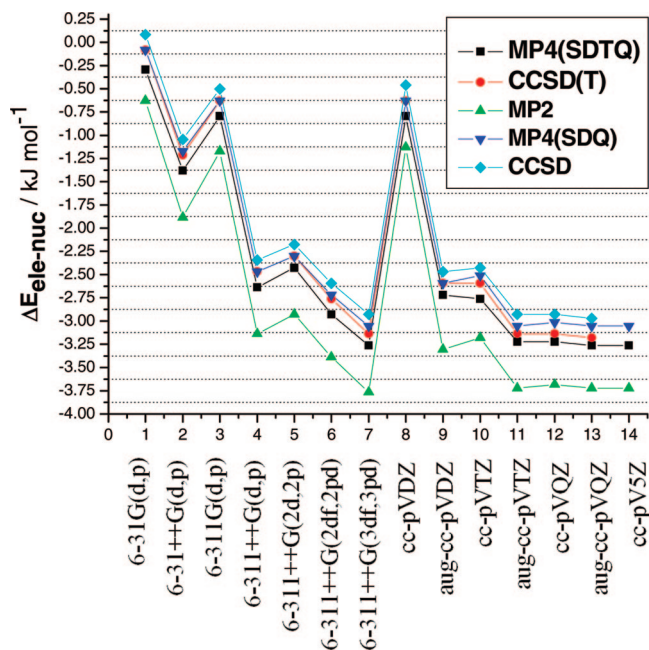


Figure 2. Anti \rightarrow gauche energy ($\Delta E_{\text{ele-nuc}}$ in the vacuum) variation for 1,2-difluoroethane as a function of the level of calculation. The CCSD(T)/6-311++G(3df,3pd)/MP2/6-311++G(3df,3pd) and CCSD(T)/aug-cc-pVQZ/MP2/aug-cc-pVTZ relative energy values are respectively -3.14 and -3.18 kJ mol^{-1} . The corresponding MP4(SDTQ) values are respectively -3.26 and -3.26 kJ mol^{-1} (the MP4(SDTQ)/cc-pV5Z/MP2/aug-cc-pVTZ value is -3.26 kJ mol^{-1}).

mol^{-1} . We have also used the G3(MP2) method,²⁸ which is known to be recommended for the energy calculation of fluorine compounds. The obtained relative energy value is

-3.05 kJ mol^{-1} , virtually the same as our CCSD(T)/6-311++G(3df,3pd) value of -3.14 kJ mol^{-1} . Therefore, the ab initio post-HF level of calculation employed here can surely be considered very adequate.

At this point, from the analysis of the theoretical results reported in Tables 1–3 and Figures 1 and 2, it can be said that any disagreement with experimental results regarding the calculation of the anti/gauche conformational population ratio cannot be attributed only to the ab initio level of theory used in the present work. It can be seen that the variation in the calculated molecular properties (structural parameters, vibrational frequencies, and relative energies) as a function of the correlated ab initio level of theory and quality of the basis set would cause a change in the conformational population values, certainly well below the corresponding experimental uncertainties (2–5%). Therefore, we are confident in using our ab initio data to analyze the performance of the theoretical models for calculating thermal corrections through the evaluation of molecular partition functions, making use of the statistical thermodynamics formalism and, therefore, enthalpy and Gibbs free-energy values, leading to the theoretical determination of conformational population ratios.

Now, we finally turn to the analysis of the ab initio temperature-dependent enthalpy and Gibbs population results for the anti \rightarrow gauche processes for 1,2-difluoroethane and 1,2-dichloroethane reported in Tables 4 and 5, with the temperature range being chosen according to the reported experimental conditions. Only the results obtained with the 6-311++G(3df,3pd) basis set and CCSD(T) level of theory are reported. Just to mention, as quoted in Tables 4 and 5, the MP2/aug-cc-pVTZ values for ΔU and ΔG_T show a very small deviation from the corresponding MP2/6-311++G(3df,3pd) values (approximately 0.1 kJ mol^{-1} at 25°C). Therefore, essentially the same conformational population is obtained using the aug-cc-pVTZ basis set.

It can be seen from Tables 4 and 5 that the effect of the anharmonic correction to the vibrational frequencies on the thermal energies, as explained in the computational section, is quite small (± 0.04 kJ mol^{-1}) and so can be neglected; therefore, only the treatment of the low-frequency modes need to be considered. It is important to make it clear that the anharmonicity effect was not included explicitly in the vibrational partition function, which can easily be done for diatomic molecules;¹⁸ however, much more work is required for polyatomic molecules. In the present case, the harmonic oscillator functional dependence was used for the vibrational partition function, but the anharmonic frequencies are utilized instead of harmonic values.

As far as enthalpy calculations are concerned, it can be seen from Table 4 that the ab initio and experimental enthalpy values for the anti \rightarrow gauche process exhibit a very fair agreement, for both 1,2-dichloroethane and 1,2-difluoroethane, independent of the way that the low-frequency modes are treated. In other words, the internal energy contribution is not so sensitive to the model used to treat the low-frequency modes in the calculation of relative enthalpy values, with the $\Delta E_{\text{ele-nuc}}$ contribution being of major relevance.

Table 4. Temperature-Dependent Enthalpy (ΔH) Values Calculated Including Anharmonicity and Hindered-Rotation Effects on the Internal Energy Correction (ΔU) Calculated at the MP2/6-311++G(3df,3pd) Level, for the anti \rightarrow gauche Interconversion Process for 1,2-Dichloroethane and 1,2-Difluoroethane^a

1,2-dichloroethane	ΔU^b	$\Delta U^{\text{True-Vibc}}$	$\Delta U^{\text{Hind-Rotd}}$	ΔH	$\Delta H^{\text{True-Vibc}}$	$\Delta H^{\text{Hind-Rot-Anhe}}$	ΔH exptl.
$T = 25\text{ }^\circ\text{C}$	-0.50	-0.96	-0.04	4.98	4.52	4.90	[5.0 \pm 0.8] ^f
$T = 40\text{ }^\circ\text{C}$	-0.50	-0.92	-0.04	4.98	4.52	4.90	
$T = 140\text{ }^\circ\text{C}$	-0.54	-0.84	-0.04	4.94	4.64	4.85	

1,2-difluoroethane	ΔU^b	$\Delta U^{\text{True-Vibc}}$	$\Delta U^{\text{Hind-Rotd}}$	ΔH	$\Delta H^{\text{True-Vibc}}$	$\Delta H^{\text{Hind-Rot-Anhe}}$	ΔH exptl.
$T = 25\text{ }^\circ\text{C}$	-0.63	-0.96	-0.08	-3.77	-4.10	-3.89	[-3.39 \pm 0.54] ^g
$T = 56\text{ }^\circ\text{C}$	-0.67	-0.96	-0.13	-3.81	-4.10	-3.97	
$T = 92\text{ }^\circ\text{C}$	-0.67	-0.96	-0.13	-3.81	-4.10	-3.97	

^a CCSD(T)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) $\Delta E_{\text{ele-nuc}}$ values (5.48 and -3.14 kJ mol⁻¹ for 1,2-dichloroethane and 1,2-difluoroethane, respectively) were used. All values are in kJ mol⁻¹. ^b The MP2/aug-cc-pVTZ ΔU values for 1,2-dichloroethane and 1,2-difluoroethane are respectively -0.50 and -0.63 kJ mol⁻¹ at 25 °C. ^c Calculated using the vibrational partition function evaluated excluding the low-frequency normal vibrational modes (three modes at room temperature). Only the true vibrational modes that can be satisfactorily described as harmonic oscillators were considered. ^d Internal rotation correction to the MP2/6-311++G(3df,3pd) internal energy term (ΔU) value (one internal rotation was identified for all four species). ^e $\Delta H^{\text{Hind-Rot-Anh}} = \Delta E_{\text{ele-nuc}} + \Delta U + \Delta U^{\text{Hind-Rot}} + \Delta U^{\text{Anh}}$. Value obtained including the anharmonicity and hindered internal rotation correction to calculation of the internal energy correction. The anharmonic correction to internal energy (ΔU^{Anh}) is -0.04 kJ mol⁻¹ for both 1,2-dichloro- and 1,2-difluoroethane, evaluated at the MP2/6-311++G(2d,2p) level and room temperature. This should be our best enthalpy value. ^f Experimental value from ref 38. ^g Experimental value from ref 8.

Table 5. Temperature-Dependent Gibbs Population (%Pop.) and Relative Gibbs Free Energy (ΔG) Values Calculated Including Anharmonicity and Hindered-Rotation Effects on the Entropy Contribution ($T\Delta S$) to the Thermal Energy Correction (ΔG_T) Calculated at the MP2/6-311++G(3df,3pd) Level, for the anti \rightarrow gauche Interconversion Process for 1,2-Dichloroethane and 1,2-Difluoroethane^a

1,2-dichloroethane	$T\Delta S^b$	$T\Delta S^{\text{True-Vibc}}$	$T\Delta S^{\text{Hind-Rotd}}$	ΔG	%Pop. anti	$\Delta G^{\text{True-Vibc}}$	%Pop. anti	$\Delta G^{\text{Hind-Rot-Anhe}}$	%Pop. anti	%Pop. exptl. anti
$T = 25\text{ }^\circ\text{C}$	-0.46	0.54	1.67	5.44	90%	3.97	83%	3.77	82%	[78 \pm 5%] ^f
$T = 40\text{ }^\circ\text{C}$	-0.46	0.63	1.76	5.44	89%	3.93	82%	3.68	81%	[77.0 \pm 1.7%] ^g
$T = 140\text{ }^\circ\text{C}$	-0.67	0.71	2.30	5.61	84%	3.93	76%	3.26	72%	[67.5 \pm 2.2%] ^g

1,2-difluoroethane	$T\Delta S^b$	$T\Delta S^{\text{True-Vibc}}$	$T\Delta S^{\text{Hind-Rotd}}$	ΔG	%Pop. anti	$\Delta G^{\text{True-Vibc}}$	%Pop. anti	$\Delta G^{\text{Hind-Rot-Anhe}}$	%Pop. anti	%Pop. exptl. anti
$T = 25\text{ }^\circ\text{C}$	-0.71	0.21	-0.17	-3.05	23%	-4.31	15%	-2.93	23%	[37 \pm 5%] ^h
$T = 56\text{ }^\circ\text{C}$	-0.84	0.25	-0.21	-2.97	25%	-4.35	17%	-2.85	26%	[41 \pm 5%] ^h
$T = 92\text{ }^\circ\text{C}$	-0.92	0.25	-0.21	-2.89	28%	-4.35	19%	-2.76	29%	[44 \pm 5%] ^h

^a CCSD(T)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) $\Delta E_{\text{ele-nuc}}$ values (5.48 and -3.14 kJ mol⁻¹ for 1,2-dichloroethane and 1,2-difluoroethane respectively) were used. All values are in kJ mol⁻¹. ^b The MP2/aug-cc-pVTZ $T\Delta S$ values for 1,2-dichloroethane and 1,2-difluoroethane are respectively -0.46 and -0.84 kJ mol⁻¹ at 25 °C. The room-temperature MP2/6-311++G(3df,3pd) rotational entropy ($T\Delta S^{\text{rot}}$) contributions are 0.46 and 0.21 kcal mol⁻¹ for 1,2-dichloroethane and 1,2-difluoroethane, respectively (identical to the MP2/aug-cc-pVTZ values). ^c Calculated using the vibrational partition function evaluated excluding the low-frequency normal vibrational modes (three modes at room temperature). ^d Internal rotation correction to the MP2/6-311++G(3df,3pd) entropy term ($T\Delta S$) value (one internal rotation was identified for all four species). ^e $\Delta G^{\text{Hind-Rot-Anh}} = \Delta E_{\text{ele-nuc}} + \Delta G_T + \Delta G_T^{\text{Hind-Rot}} + \Delta G_T^{\text{Anh}}$, ($\Delta G_T = \Delta U - T\Delta S$). Values obtained include the anharmonicity and hindered internal rotation correction to the calculation of the thermal energy correction (ΔG_T). The anharmonic correction to entropy ($T\Delta S^{\text{Anh}}$) is -0.08 kJ mol⁻¹, for both 1,2-dichloro- and 1,2-difluoroethane, evaluated at the MP2/6-311++G(2d,2p) level and room temperature. This should be our best Gibbs free-energy value. ^f Experimental value from ref 4. See also ref 38. ^g Experimental value from ref 40. ^h Experimental value from ref 8. There are two other population datapoints obtained from an electron diffraction experiment that differ considerably from the more recent reported value in ref 8 based on the vibrational spectroscopy analysis: 9% of the anti form from ref 41 at room temperature and 4.0 \pm 1.8 at 22 °C from ref 42.

Regarding 1,2-dichloroethane, Ayala and Schlegel¹⁹ have shown that the hindered-rotor approach would be appropriate in the evaluation of the vibrational partition function using the HF/6-31G(d) level of calculation,³⁹ which is also corroborated by the results reported here. In the present article, comparisons with experimental results are made for conformational populations, which were determined experimentally with a satisfactory precision, and calculated at the ab initio level using a specific vibrational partition function containing a treatment of the low-frequency modes reported by Ayala and Schlegel¹⁹ (implemented in the Gaussian package³³). Then, when the agreement between theoretical and experimental populations is analyzed,

an assessment of the performance of the hindered-rotor approach can be made. From Table 5, the effectiveness of the hindered-rotor approach to describe the 1,2-dichloroethane species is promptly seen, leading to a good agreement with gas-phase electron diffraction conformational population data. The simple procedure of neglecting the low-frequency modes (three modes at room temperature) in the evaluation of the vibrational partition function, which may be considered as a rough but simple approximation, used successfully in the conformational analysis of cyclooctane^{43,44} and cycloheptane,⁴⁵ also works well for 1,2-dichloroethane up to a temperature of 40 °C.

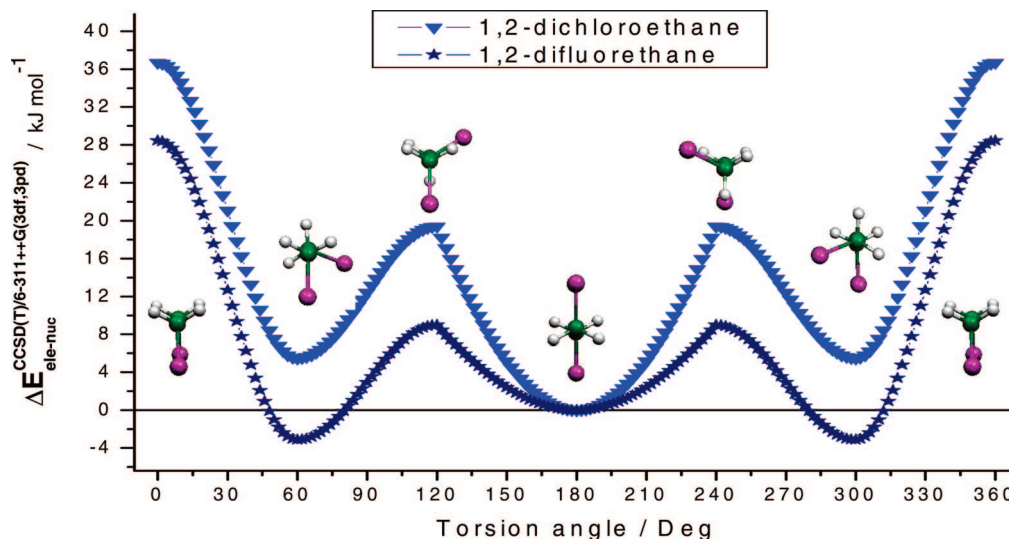


Figure 3. CCSD(T)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) relative energies (in units of kJ mol^{-1}) for the four stationary points located on the MP2/6-311++G(3df,3pd) PES for 1,2-dichloroethane and 1,2-difluoroethane: **anti** minimum, **TS1** structure, **gauche** minimum, **TS2** structure. The room temperature V_0/kT barrier values are 32.6 kJ mol^{-1} (anti \rightarrow gauche process) and 20.5 kJ mol^{-1} (gauche \rightarrow anti process), respectively, for the chlorine and fluorine species ($1 \text{ cal} = 4.184 \text{ J}$; $1 \text{ kcal mol}^{-1} = 349.38 \text{ cm}^{-1}$).

For 1,2-difluoroethane, a satisfactory agreement with experimental conformational population data was not obtained. An interesting feature that can be seen from Table 5 is the fact that the procedure of treating the lowest-frequency modes as a hindered rotor leads to a very small correction, compared to the corresponding value obtained for 1,2-dichloroethane, providing virtually the same conformational population as the consideration of all 3N-6 modes as harmonic oscillators. So, in this case, the procedure was useless. The alternative of ignoring the three lowest-frequency modes also does not work well here, similar to the case of the cyclononane molecule.⁴⁶

The calculated CCSD(T)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) potential barriers (V_0) are shown in Figure 3 for the anti \leftrightarrow TS1 \leftrightarrow gauche and gauche \leftrightarrow TS2 \leftrightarrow gauche processes. It can be seen from Figure 3 that the energy barrier for anti \rightarrow gauche interconversion is 19.2 (13.8) kJ mol^{-1} for 1,2-dichloroethane and 12.1 (9.2) kJ mol^{-1} for the gauche \rightarrow anti interconversion in 1,2-difluoroethane (the values in parenthesis are for the reverse process). The corresponding barriers for the interconversion between two equivalent gauche structures are 31.4 and 31.8 kJ mol^{-1} respectively for 1,2-dichloroethane and 1,2-difluoroethane. The gauche \rightarrow anti barrier for the fluorine species is 7.1 kJ mol^{-1} (4.6 kJ mol^{-1} for the reverse barrier) smaller than the anti \rightarrow gauche barrier for 1,2-dichloroethane. The experimental barriers reported for 1,2-difluoroethane⁸ are 8.87 (anti \leftrightarrow TS1 \rightarrow gauche) and $23.93 \text{ kJ mol}^{-1}$ (gauche \rightarrow TS2 \rightarrow gauche). The former is close to the CCSD(T)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) calculated value (12.1 kJ mol^{-1}), whereas the latter is predicted to be 31.8 kJ mol^{-1} , a deviation of almost 8 kJ mol^{-1} . At temperatures such that $V_0 \ll kT$ (where k is the Boltzmann constant and T the absolute temperature), the internal rotation is essentially free and can be treated by methods similar to those for the rigid rotor, and when $V_0 \gg kT$, the molecule is trapped at the

bottom of the potential well and the motion is that of a simple torsional vibrational, which can be treated by a method similar to that used for the simple harmonic oscillator. For intermediate V_0 values, as the ones reported in this work for 1,2-difluoroethane ($V_0/kT = 20.5 \text{ kJ mol}^{-1}$) and 1,2-dichloroethane ($V_0/kT = 32.6 \text{ kJ mol}^{-1}$), at room temperature, the motion is intermediate between that of a free rotation and that of torsional vibration. In this work, we used a modified hindered rotor partition function for the lowest-frequency vibrational mode proposed by Ayala and Schlegel,¹⁹ which has a dependence on V_0/kT , as previously reported by Pitzer and Gwinn.²⁹ We assumed that the molecular vibrational partition function (q^{vib}) can be written as a product of harmonic oscillator (HO) and hindered rotor (Hind-Rot) contributions according to eq 6, and so the thermodynamic functions are obtained as a sum of two terms, and then the hindered rotor correction is analyzed.

$$q^{\text{vib}} = q^{\text{HO}} q^{\text{Hind-Rot}} \quad (6)$$

Looking at the individual values for the hindered rotor correction, it can be seen that the problem is with the gauche form of 1,2-difluoroethane. For 1,2-dichloroethane, the values of the respective corrections for entropy contribution are $\text{TS}_{\text{anti}}^{\text{Hind-Rot}} = 0.17$ and $\text{TS}_{\text{gauche}}^{\text{Hind-Rot}} = 1.84 \text{ kJ mol}^{-1}$. However, for 1,2-difluoroethane, the values are rather different, with the correction for the gauche structure being even less than that for the anti form, that is, $\text{TS}_{\text{anti}}^{\text{Hind-Rot}} = 0.33$ and $\text{TS}_{\text{gauche}}^{\text{Hind-Rot}} = 0.17 \text{ kJ mol}^{-1}$. Therefore, it appears that the hindered rotor correction for the 1,2-difluoroethane gauche conformer should be similar to that for the 1,2-dichloroethane (around 1.67 kJ mol^{-1}), however, having a negative value. We cannot say for sure if only the variation in V_0 with respect to 1,2-dichloroethane affects so much the hindered rotor partition function given in ref 19 to the point of making the agreement with experimental conformational population so poor.

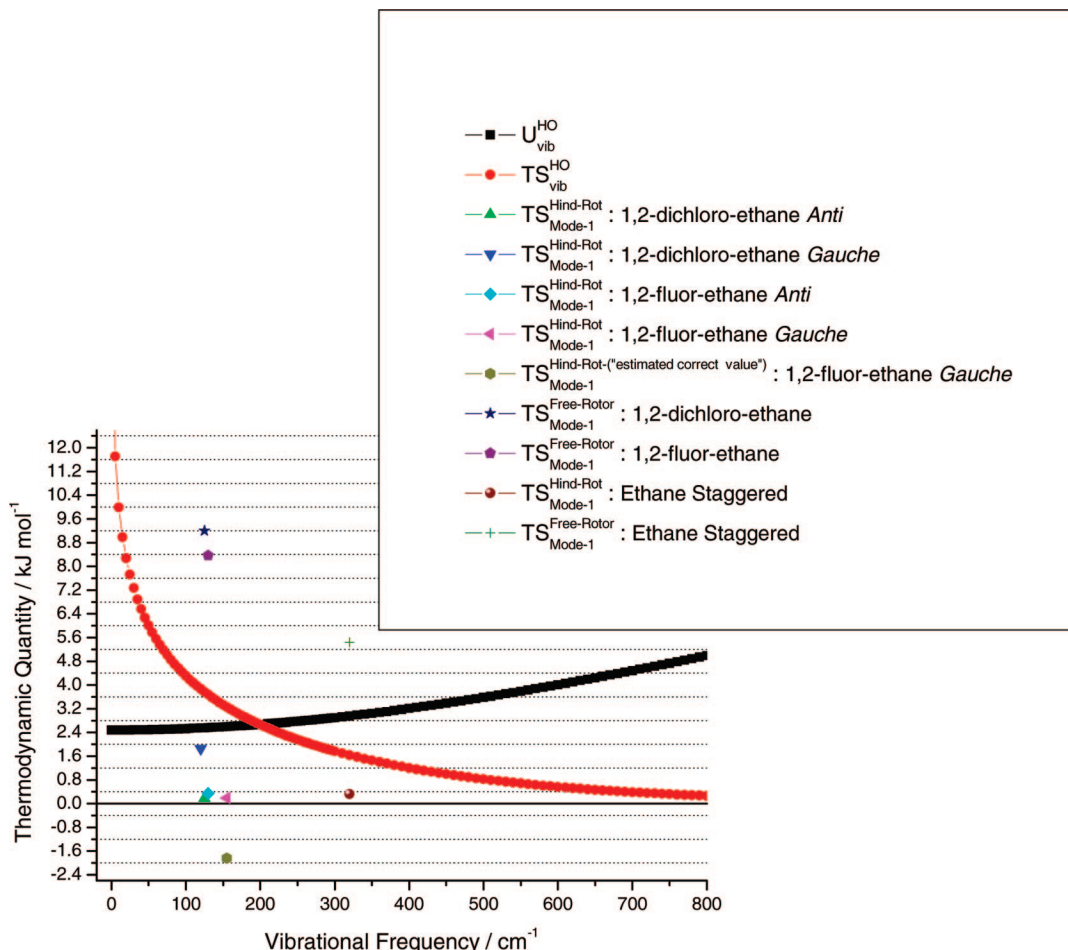


Figure 4. Thermodynamic energy or internal thermal energy (U) and entropic (TS) vibrational contributions (in units of kJ mol^{-1}) represented as a function of the vibrational frequency, calculated with the aid of the statistical thermodynamics formulas, within the harmonic oscillator (HO) approximation (HO vibrational partition function), at room temperature and normal pressure. The specific TS vibrational contribution due to the lowest frequency mode, using a hindered-rotor partition function and free-rotor approach is also shown for ethane, 1,2-chloro- and 1,2-difluoroethane (MP2/6-311++G(3df,3pd) value).

With the aim of clarifying the reason for the disagreement between theoretical and experimental gas-phase conformational population for 1,2-difluoroethane, we decided to use the experimental entropy for the anti \leftrightarrow gauche process, obtained from the analysis of the vibrational spectral data dependence with temperature reported in ref 8, where by applying the van't Hoff isochore equation the entropy change for the process could be evaluated. The experimental entropy contribution at room temperature is $T\Delta S^{\text{Expt}} = -2.05 \text{ kJ mol}^{-1}$. Our MP2/6-311++G(3df,3pd) best value is $-0.71 \text{ kJ mol}^{-1}$ (a quite sizable 65% difference). Using the experimental entropy and our ab initio CCSD(T)/6-311++G(3df,3pd) relative energy ($\Delta E_{\text{ele-nuc}}$) and MP2/6-311++G(3df,3pd) internal energy (ΔU), we obtain a room-temperature Gibbs population of 33% of the anti form, in good agreement with the experimental value of $37 \pm 5\%$. Therefore, it is quite evident that our calculated entropy for the anti \leftrightarrow gauche process of 1,2-difluoroethane, using the combined quantum mechanical/statistical thermodynamic approach, is in serious error. It is well-known that the entropy term ($T\Delta S^{\text{vib}}$) has a much higher sensibility to the low-frequency mode than the internal energy (ΔU^{vib}), which can be easily seen from Figure 4, where the variation of the respective

thermodynamic functions with the vibrational frequency is shown. ΔU^{vib} is very monotonically dependent on the frequency in the low-frequency region, which explains why our calculated enthalpies are in good agreement with the experimental ones. On the contrary, the entropy counterpart is strongly dependent on the frequency in the region of 0–200 cm^{-1} ; therefore, the treatment of low-frequency modes definitively has a pronounced effect on the entropy evaluation. When we used the experimental entropy for the gauche \rightarrow anti process (1,2-difluoroethane) instead of the calculated one using the hindered rotor approach, the agreement with experimental results is fine. This is irrefutable proof that the calculated $T\Delta S^{\text{vib}}$ entropy contribution to the Gibbs free energy (ΔG) is poorly described, and it becomes evident that this is the major reason for the serious disagreement with the experimental determination of the conformational population for the 1,2-difluoroethane. Also shown in Figure 4 is the individual hindered-rotor corrections for each conformer (anti and gauche) and also for the ethane molecule only, for reasons of comparison.

The calculated ab initio (MP2/6-311++G(3df,3pd) value) TS^{vib} contribution due to the first low-frequency mode for the individual anti and gauche forms of 1,2-dichloro- and

1,2-difluorethane, and also the ethane molecule (*staggered* conformation), evaluated using the hindered-rotor approach from ref 19 (named $TS^{\text{Hind-Rot}}$) and also considering the first vibrational mode as a free rotor ($TS^{\text{Free-Rotor}}$) are highlighted in Figure 4 (the free-rotor contribution is the same for the anti and gauche forms, since there is no barrier for rotation, so the effect on the entropy difference is null, which is equivalent to just ignoring the first low-frequency mode in the evaluation of the vibrational partition function). The hindered-rotor correction for the anti form of the fluor and chlorine species is almost the same. However, for the gauche form, the correction for the chlorine is quite different from the fluorine species, which practically has no variation at all, as already mentioned before. Then, the contribution of the hindered rotation to entropy is virtually zero for the 1,2-difluorethane, and this can be a reason for the disagreement with experimental results. Analyzing the rotational constants and spatial orientations with respect to the principal axis coordinate system, and using the rotational entropy data for CH_3Cl and CH_3F and the corresponding values for $^{\bullet}\text{CH}_2\text{Cl}$ and $^{\bullet}\text{CH}_2\text{F}$ radicals as a model for a free rotating group, assuming the first low-frequency mode as a free rotor, we estimated the contribution to the vibrational entropy ($TS^{\text{Free-Rotor}}$) to be ~ 9.2 and 8.4 kJ mol^{-1} respectively for the chlorine and fluorine species. In the case of the ethane molecule, when the rotational entropy data for CH_4 and the $^{\bullet}\text{CH}_3$ radical is used for modeling the free rotating CH_2 group, the free rotor value for the first vibrational mode is estimated to be $\sim 5.4 \text{ kJ mol}^{-1}$. Therefore, there is no point in considering the internal rotation mode as a free rotor, in the case of 1,2-difluorethane. The sizable difference in the energy barrier for internal rotation between the chlorine ($V_0 = 19.2 \text{ kJ mol}^{-1}$) and fluorine ($V_0 = 12.1 \text{ kJ mol}^{-1}$) species (anti \rightarrow gauche and gauche \rightarrow anti processes respectively) would probably make a contribution to the poor performance of the hindered rotor partition function in the case of 1,2-difluorethane, and consequently a visible disagreement with experiment, regarding the anti/gauche conformational population ratio values. However, we cannot quantify the extent of this effect. We may just speculate that the vibrational partition used in this work may have an inadequate dependence on the V_0/kT value, which could make it unsuitable for substituted ethane molecules exhibiting the gauche effect, such as 1,2-difluorethane. If only the lowest-frequency mode is ignored, essentially the same result is obtained when it is considered a harmonic oscillator in the vibrational partition function for 1,2-dichloroethane, corroborating that it should be treated separately as a hindered rotor, and not just disregarded, where, as can be seen in Figure 4, it adds a substantial correction to the anti/gauche entropy difference ($T\Delta S^{\text{Hind-Rot}} = 1.67 \text{ kJ mol}^{-1}$) and therefore conformational population. Nevertheless, the same reasoning does not apply to 1,2-difluorethane, where the treatment of the first vibrational normal mode as a hindered rotor did not make any noticeable difference ($T\Delta S^{\text{Hind-Rot}} = -0.17 \text{ kJ mol}^{-1}$). For the ethane molecule, the effect due to the hindered rotation is also small ($TS^{\text{Hind-Rot}} = 0.31 \text{ kJ mol}^{-1}$; $S^{\text{Hind-Rot}} = 1.05 \text{ J mol}^{-1} \text{ K}^{-1}$), but improving the deviation from experimental

results from 1% to 0.5%. So, in this well-known case, the hindered-rotor model works perfectly well.

It is also opportune to emphasize here that, as already pointed out by Ayala and Schlegel,¹⁹ in principle, most of the problem resides in the identification of the internal rotation modes. Large molecules can have a large number of low-frequency modes which can include not only internal rotations but also large amplitude collective bending motions of atoms. Moreover, some of the low-frequency modes can be a mixture of such motions. In the case of cyclic molecules featuring rings bigger than six members in size, there are ring torsional modes, and similar to internal rotations, ring torsions can cause problems in the evaluation of thermodynamic functions (see for example refs 44–46). For simple systems such as substituted ethane molecules, it is possible to unambiguously identify the low-frequency internal rotation modes and also use an adequate ab initio correlated level of theory, with a good quality basis set, to provide equilibrium geometries and vibrational frequencies necessary for the evaluation of partition functions, and also relative energy values, for the calculation of thermodynamic quantities. In this case, an assessment of the performance of approximated methods available to predict conformational populations can be made.

4. Conclusions

It is usually assumed that the standard statistical thermodynamics formalism can be safely applied once the quality of the distinct energy values, which are necessary for the evaluation of partition functions, is assured by the use of accurate quantum chemical methods. In this work, we used the best computational affordable quantum chemical methods in the calculation of geometrical parameters and harmonic frequencies (MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ), required for the evaluation of rotational and vibrational partition functions (and therefore thermal correction, ΔG_T), and highly correlated post-HF calculations (CCSD(T)/6-311++G(3df,3pd) and CCSD(T)/aug-cc-pVQZ) of relative energies ($\Delta E_{\text{ele-nuc}}$), required for the theoretical calculation of Gibbs free energies (ΔG) and, therefore, conformational population values. We selected two substituted ethane molecules, where for one of them (1,2-difluorethane) the gauche effect is known to be operating. In the calculation of thermal corrections, we used a hinder-rotor treatment for the low-frequency mode and also anharmonicity correction to the vibrational frequencies within the harmonic oscillator partition function. The agreement with gas-phase experimental data was fine for 1,2-dichloroethane; however, reasonable accordance with experimental results was not obtained in the case of 1,2-difluorethane. The cause of the disagreement with the experimental conformational population ratio is not the ab initio level of calculation employed, since we analyzed the behavior of the methodology as a function of level of theory and size of the basis set and could guarantee that, by improving the level of calculation to a computational unreachable degree of sophistication, no significant variation of the conformational population would be observed. Therefore, the results reported here show definitively that the problem of the agreement with experi-

ment is related to the treatment used for the low-frequency vibrational modes. The inclusion of anharmonic corrections (using anharmonic frequencies and the harmonic oscillator partition function) and a treatment of low-frequency modes as a hindered rotor for the evaluation of the thermal correction ($\Delta G_T^{\text{Hind-Rot-Anh}}$) did not improve the agreement with experimental results regarding conformational population values, in the case of 1,2-difluoroethane. The lower gauche \rightarrow anti interconversion energy barrier found for 1,2-difluoroethane, compared to that for 1,2-dichloroethane (anti \rightarrow gauche), may contribute to the poor performance of the hindered rotor partition function; however, we cannot quantify its extent nor how important the gauche effect is for the whole affair.

It is interesting to point out that a great part of the molecular systems of interest to a number of quantum chemists, using standard computer codes (freely delivered or not) where the quantum mechanical and statistical thermodynamics formalism are readily implemented in the calculation of thermodynamic properties, may have peculiarities that can easily be overlooked. In this case of substituted ethane molecules, only three low-frequency modes are present, and therefore, a theoretical, sound, and adequate computational model is available or can be pursued. However, for large molecular systems, a considerable number of low-frequency modes are certainly present, and use of the harmonic oscillator partition function is not advised. So, in this case, finding a satisfactory computational treatment is indeed a hard task. Fortunately, in many situations, energy differences are calculated, and so, a cancelation of errors is often present. Then, the effect of the low-frequency modes may be of small importance, mainly when the size of the relative energy value ($\Delta E_{\text{ele-nuc}}$) is much larger than the thermal energy correction.

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