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LETTERS

Conformational Stability of 3-Fluoropropene: A Challenging Problem for Both Theory and Experiment

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Experiments have shown the cis conformer of 3-fluoropropene to lie lower in energy than the gauche conformer, with enthalpy differences ranging from 58 to 263 cm^{-1} depending upon the experimental method. Van der Veken, Herrebout, Durig, Zhao, and Durig have studied this system at the MP2 level. While their MP2/6-311G(d,p) results, predicting an enthalpy difference of 192 cm^{-1}, agreed with the experimental evidence, their highest level of theory, MP2/6-311++G(d,p), gave a reversed energetic ordering, predicting the gauche conformer to be more stable by 117 cm^{-1}. We have used much larger basis sets to resolve this discord between theory and experiment. Systematic basis set trends are observed in our results. In particular, the inclusion of diffuse functions with small basis sets significantly increases the stability of the gauche conformer relative to the cis conformer, sometimes resulting in an incorrect energetic ordering. This effect is greatly reduced with larger basis sets. Our highest level results agree qualitatively with experimental conclusions, predicting the cis conformer to lie lower by 40 and 21 cm^{-1} at the MP2/cc-pVQZ and MP2/aug-cc-pVQZ levels, respectively. Entropy considerations are seen to be very important.

I. Introduction

Various experimental techniques including infrared, Raman, microwave, and NMR spectroscopies have been applied in studying the conformational isomerism of 3-fluoropropene, $CH_2{=}CH{-}CH_2{-}F$.[1−11] 3-Fluoropropene exists as a mixture of cis and gauche rotamers in the gas phase at ambient temperature. Experimental observations have shown the cis conformer to be the energetically lower lying isomer. The experimental enthalpy difference between the two rotamers in the gas phase varies considerably with different methods: from 58 ± 23 cm^{-1} (694 ± 120 J/mol) in microwave studies to 263 ± 25 cm^{-1} (3.15 ± 0.3 kJ/mol) from the temperature dependence of the Raman spectrum. In a recent study Van der Veken, Herrebout, Durig, Zhao, and Durig[12] determined the enthalpy difference between the more stable cis conformer and the higher energy gauche conformer of $CH_2{=}CH{-}CH_2{-}F$ in rare gas solutions to range from 60 ± 8 cm^{-1} for liquid xenon to 81 ± 1 cm^{-1} (969 ± 12 J/mol) for liquid argon. These values were extrapolated to 130 ± 25 cm^{-1} for the gas phase. Although it is obvious that the cis−gauche energy difference is small, the discrepancies between the different experiments is troubling.

The authors of the recent experimental paper have also performed theoretical studies of the conformational equilibrium at different levels of *ab initio* molecular orbital theory.[12] The experimental and theoretical literature results are summarized

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TABLE 1: Existing Literature Data for Experimental and Theoretical Values of the Enthalpy Difference (cm^{-1}) between the Cis and the Gauche Conformers of 3-Fluoropropene

method	state	$\Delta H(\Delta E)$	ref
Raman	liquid	58 ± 10	4
microwave	gas	58 ± 23	1
microwave/far-infrared	gas	108	2
Raman	gas	263 ± 25	4
infrared	matrix	211 ± 25	8
far-infrared	gas	130 ± 25	12
MP2/6-311G(d,p)		192	12
MP2/6-311++G(d,p)		−117	12

A positive energy difference indicates that the cis structure lies lower in energy.

in Table 1. Notably, as compared to the experimental data, the MP2/6-311++G(d,p) level of theory reversed the energetic ordering of the conformers of 3-fluoropropene. Computations at this level, while producing structural parameters in better agreement with experiment than other methods used, predicted the gauche conformer to be more stable by 117 cm^{-1} (1.40 kJ/mol).[12] The apparent contradiction in the theoretical results is quite interesting though not entirely surprising. Conformational equilibria with very low energy differences are usually difficult to predict,[13,14] especially in quantitative terms. Considering the advanced state of contemporary computational quantum chemistry, however, the resolution of such apparent discords between theory and experiment is of obvious interest.

In the present study we apply electronic structure theory incorporating larger basis sets and more reliable methods of recovering electron correlation to resolve the controversy related to the thermodynamic stability of the rotamers of 3-fluoropropene.

II. Computational Methods

A range of basis sets was explored in the present study. Specifically, Dunning's correlation consistent basis sets cc-pV*X*Z ($X = 2-4$)[15,16] were employed as well as basis sets constructed from the 6-311G platform of Krishnan, Seeger, Binkley, and Pople[17] and the polarization and diffuse functions of Frisch, Pople, and Binkley[18] and Clark, Chandrasekhar, and Schleyer.[19] Dynamic electron correlation was accounted for through Möller−Plesset second-order perturbation theory (MP2)[13,20,21] for all basis sets and via the quadratic configuration interaction method including all single and double excitations (QCISD)[22] for the four smallest basis sets. The four core molecular orbitals were frozen for all methods. The *ab initio* computations were performed with the Gaussian 94 program package.[23]

For the five smallest basis sets, harmonic vibrational frequencies were evaluated at the MP2 level and used to compute zero-point energy corrections. All geometries were fully optimized with the exception of the MP2/aug-cc-pVQZ level of theory. Gradient calculations with this basis set (550 contracted Gaussian functions) were impractical with our computing resources. MP2 single-point energies were determined at both the MP2/cc-pVQZ and MP2/aug-cc-pVTZ optimized geometries. Enthalpy differences evaluated from MP2/aug-cc-pVQZ single-point energies at both sets of optimized geometries agreed to within 1 cm^{-1}.

III. Results and Discussion

In a recent study Csaszar, Allen, and Schaefer[14] examined the *ab initio* limits of conformational energy estimates by carrying out extensive computations at various levels of theory for a number of small molecules. The results obtained have demonstrated the complexity in the quantitative predictions of the thermochemistry of large amplitude molecular motions. The theoretical methods tested were Möller−Plesset perturbation theory from second to fifth order[13,20,21] and the coupled cluster[24] methods CCSD,[24,25] CCSD(T), and CCSDT.[26] Atomic-orbital basis sets from moderate size to as large as [7s6p5d4f3g2h1i/6s5p4d3f2g1h] were used. The inversion barriers of water, ammonia, and isocyanic acid, the torsional barrier of ethane, and the *E*/*Z* rotamer separation in formic acid were theoretically estimated. The latter study produced results that are far superior to the usually accepted chemical accuracy of 1 kcal/mol and show the way to quantitative predictions of spectroscopic accuracy in theoretical conformational analyses. In the present work the size of 3-fluoropropene and the low symmetry (C_1) of the gauche conformer placed constraints on the levels of theory which could be used.

TABLE 2: Theoretically Estimated Enthalpy Difference (cm^{-1}) between the Cis and Gauche Conformers of 3-Fluoropropene

method	$\Delta H(\Delta E)$	ref
MP2/6-311G(d,p)	192	12
MP2/6-311++G(d,p)	−117	12
MP2/6-311G(3d,3p)	212 (206)	this work
MP2/6-311++G(3d,3p)	7 (3)	this work
MP2/cc-pVDZ	320 (298)	this work
MP2/aug-cc-pVDZ	−55 (−50)	this work
MP2/cc-pVTZ	113 (111)	this work
MP2/aug-cc-pVTZ	11	this work
MP2/cc-pVQZ	40	this work
MP2/aug-cc-pVQZ	21	this work[b]
QCISD/6-311G(d,p)	220	this work
QCISD/6-311++G(d,p)	−50	this work
QCISD/cc-pVDZ	343	this work
QCISD/aug-cc-pVDZ	11	this work
experiment	58−263	1, 2, 4, 8, 12

[a] Zero-point vibrationally corrected values are given in parentheses where available. A positive energy difference indicates that the cis structure lies lower in energy. [b] Single-point energies were evaluated at the MP2/aug-cc-pVTZ optimized geometry.

The enthalpy differences predicted by theory are given in Table 2. The available vibrational zero-point energy corrections do not have a substantial effect on the predicted enthalpy differences. With the exception of the 22 cm^{-1} correction found at the MP2/cc-pVDZ level, these corrections are at most 6 cm^{-1}.

In contrast to results found at lower levels of theory, MP2 predictions incorporating sufficiently large basis sets are in harmony with experimental observations. Our most reliable predictions for the enthalpy difference between these conformers are 40 and 21 cm^{-1}, found at the MP2/cc-pVQZ and MP2/aug-cc-pVQZ levels of theory, respectively. Given the extraordinarily small value for this enthalpy difference, these values show agreement with the experimentally determined range of 58 ± 23 to 263 ± 25 cm^{-1}. It is important at this point to emphasize that this energy difference is far below the 1 kcal/mol (350 cm^{-1}) threshold that current quantum chemical methods typically strive toward. With this in mind one should be careful not to place undue confidence in the quantitative accuracy of these results. Optimized geometric parameters obtained at the MP2/cc-pVQZ level are shown in Figure 1.

The predicted enthalpy differences are best understood when examined in relation to basis set quality. With some exceptions, two general trends are observed in our results. When considering basis sets without diffuse functions [6-311G(d,p), 6-311G(3d,3p), cc-pVDZ, cc-pVTZ, and cc-pVQZ] a decrease in the

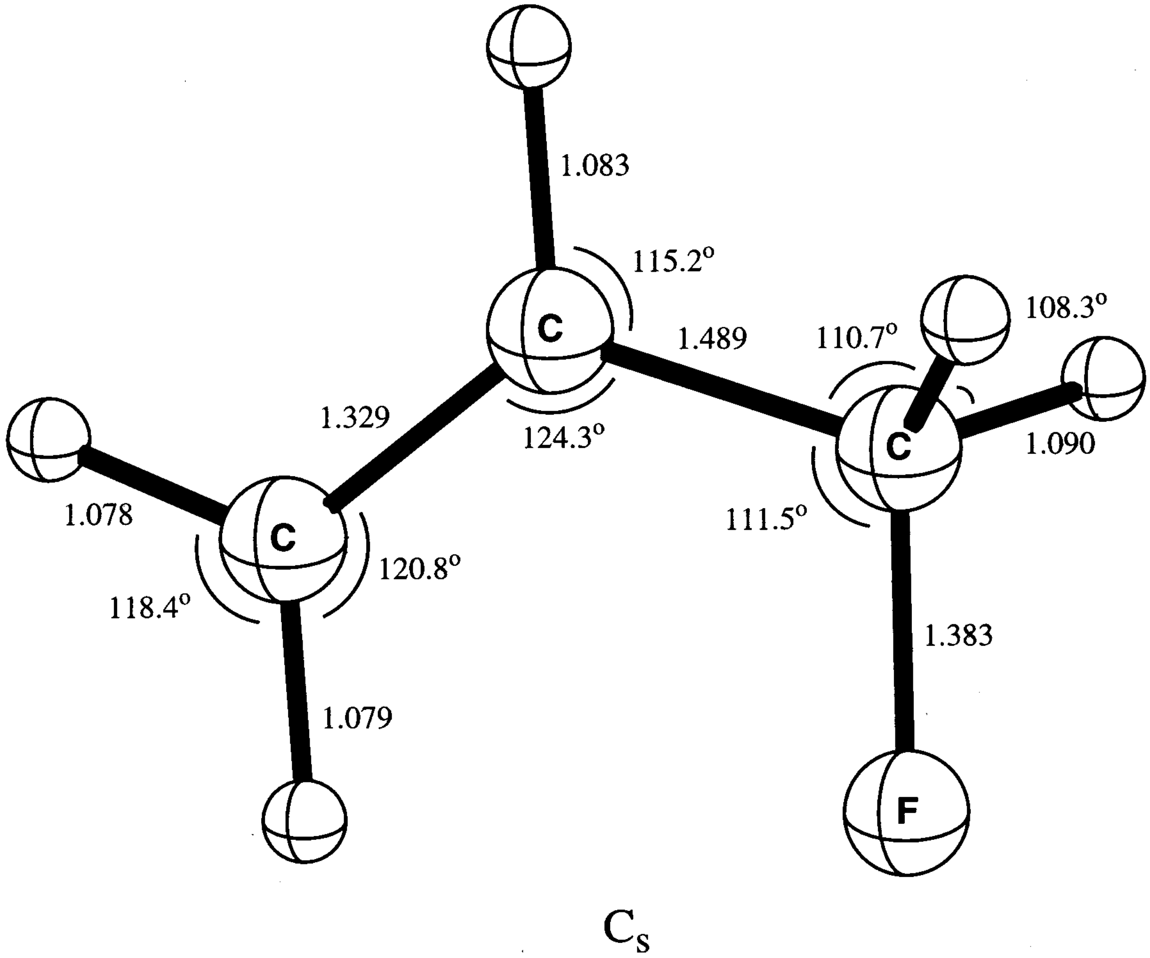

Figure 1. MP2/cc-pVQZ optimized geometric parameters for the cis conformer. Bond distances are given in angstroms.

enthalpy difference is seen as basis set size is increased. The addition of diffuse functions to the above series of basis sets [6-311++G(d,p), 6-311++G(3d,3p), aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ] is found to systematically lower the energy of the gauche conformer relative to the cis conformer. For several methods incorporating small basis sets [MP2/6-311G(d,p), QCISD/6-311G(d,p), and MP2/cc-pVDZ] this effect is so large that it reverses the energetic ordering of the conformers, as reported previously by Durig et al. at the MP2/6-311G(d,p) level.[12]

The series of correlation consistent basis sets clearly shows that the effect of diffuse functions is drastically reduced as basis set quality increases. Addition of diffuse functions to the cc-pVDZ basis set (81 → 137 contracted functions) shifts the enthalpy difference by 375 cm^{-1}, resulting in a reversed energy ordering when compared to experiment. In contrast, the addition (370 → 550 contracted functions) of diffuse functions to the cc-pVQZ basis set shifts the enthalpy difference by only 19 cm^{-1} and does not change the relative ordering of the conformers.

The enthalpy differences predicted by the QCISD and MP2 methodologies with identical basis sets demonstrate that in this case the particular method used to recover electron correlation effects does not have a significant impact on the observed basis set trends. While there are quantitative differences between results from the two methods, the only qualitative difference is that adding diffuse functions to the cc-pVDZ basis set at the QCISD level, while lowering the enthalpy difference by 332 cm^{-1}, does not change the relative ordering of the conformers. In each case QCISD lowers the energy of the cis conformer with respect to the gauche conformer. The cis lowering ranges from 23 cm^{-1} with the cc-pVDZ basis set to 67 cm^{-1} with the 6-311++G(d,p) basis set.

It is clear from our results that in order to predict enthalpy differences for this system with any confidence large basis sets must be employed. For the smallest basis sets [6-311G(d,p), cc-pVDZ] the inclusion of diffuse functions has such a large effect that the results cannot be considered reliable. For moderately sized basis sets [6-311G(3d,3p), cc-pVTZ] the effect of diffuse functions is still significant but does not reverse the energetic ordering. The decreasing effect of added diffuse functions as basis set size is increased and the small change in enthalpy differences between the cc-pVQZ and aug-cc-pVQZ basis sets permit the cautious conclusion that the MP2/cc-pVQZ and MP2/aug-cc-pVQZ results yield reasonably accurate predictions of the enthalpy difference in question. In agreement with experiment, our highest levels of theory indicate that the cis and gauche conformers have a very small enthalpy difference, with the cis conformer lying slightly lower in energy. To be more specific, our predicted ΔE (gauche-cis) $= 21$ cm^{-1} for MP2/aug-cc-pVQZ seems close to the MP2 basis set limit. The small positive increment anticipated (from our MP2 → QCISD comparisons) due to higher order correlation effects places the theoretical predictions in the middle of the experimental ΔE values. The counterintuitive sign of the gauche−cis energy difference, particularly with the involvement of fluorine, remains open to qualitative explanation. At present, this result seems to be the result of a subtle interplay of several factors.

The question of the "stability" of the gauche and cis conformers in a more general sense is interesting. Because the gauche rotamer has two forms, $-T\Delta S = -TR \ln 2 = 1700$ J/mol to a reasonable approximation. This term outweighs an energy difference of up to 142 cm^{-1}. Thus the gauche rotamer would be more abundant for many of the energy differences reported in this paper.

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