Scaled Quantum Chemical Force Fields for 1,1-Difluorocyclopropane and the Influence of Vibrational Anharmonicity

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Potential functions and harmonic (ω_i) and anharmonic (ν_i) fundamental frequencies have been calculated for 1,1-difluorocyclopropane (DFCP) and its d_4 and d_2 isotopomers using the program Gaussian 03. B3LYP and MP2 models were employed, each with the bases 6-311++G** and cc-pVTZ. Anharmonicity corrections $\Delta_i = \omega_i - \nu_i$ are listed and shown to be different for symmetric and antisymmetric CH stretching modes in situations where Fermi resonance appears to be absent. The same effect is missing in C_2H_4, for which similar calculations were made. The quadratic force fields for DFCP have been scaled in symmetry coordinate space with 15 scale factors both to observed frequencies ν_{obsd} and also to ω_{obsd}, where $\omega_{obsd} = \nu_{obsd} + \Delta$. With ν_{obsd} especially, different scale factors are needed for the symmetric and antisymmetric CH stretching force constants due to their differing anharmonicities. The source of the latter in the quartic and cubic force field is explored. MP2 calculations of valence interaction force constants involving the stretching of bonds on a common carbon atom are preferred to those from a B3LYP model. In either model, scaling to ω_{obsd} rather than to ν_{obsd} does not remove the necessity of varying scale factors for differing types of motion in the same group. Theoretical values of the five quartic centrifugal distortion constants are listed for the normal species and compared with new experimental data. The predictions are sufficiently good to be useful in fitting pure rotational transitions. A weakness is identified in the current Gaussian 03 code for the calculation of vibration−rotation quantities, and limitations are noted in the manner in which Fermi resonance is handled.

1.Introduction

Infrared and Raman spectra of three isotopomers of 1,1-difluorocyclopropane (DFCP) were recently reported in conjunction with quantum chemical (QC) studies, information from which was combined with experimental rotational constants for a number of isotopomers to yield the semi-experimental equilibrium geometry of the molecule.[1] A primary object of the present paper is to describe the force fields involved in these calculations. One role of these force fields had been to permit the calculation of the vibration−rotation interaction (alpha) constants needed to adjust ground-state rotational constants to equilibrium "state" values and to compute quartic centrifugal distortion constants.

The procedure followed in the determination of these force fields, for a molecule for which a CCSD(T) type of approach was impractical, was the established one of scaling the QC-based harmonic (quadratic) force field to reproduce observed fundamental frequencies, in our case according to the procedure of Pulay et al.[2] Such a procedure, in addition to providing a complete set of diagonal and off-diagonal quadratic force constants, has proved in many instances to be a useful means for locating missing fundamental bands, correcting misassignments, and identifying or assessing the extent of Fermi resonances. One area of the spectrum where such estimates of Fermi resonance (FR) are much to be desired is that involving the stretching of C−H bonds in CH_2 or CH_3 groups in the region of 2800−3200 cm^{-1}. In this region, the potential for obtaining information about the strengths of individual C−H bonds is great,[3] but the same region is notorious for the plethora of Fermi resonances to be found there. The need for a quantitative interpretation based on QC information is therefore acute.

A number of such studies have been made by scaling either DFT (B3LYP)- or MP2-based force fields to observed (anharmonic) frequencies with, however, conflicting results, especially in the CH stretching region.[4] These outcomes are due to a systematic difference in the value of the valence interaction force constant f' coupling the stretching of two C−H bonds sharing a common carbon atom. The B3LYP-based value of f' is always larger than the MP2 one, a feature of other bonds involving a common carbon atom.[4] This difference has the consequence that MP2 predictions of the position of the symmetric CH_2 or CH_3 stretching frequency are found to be lower than those from a B3LYP model. A MP2 calculation therefore yields rather larger Fermi resonance shifts on this mode from the usual interaction with binary levels below. The excessive size of these MP2-based Fermi resonance shifts has been used as evidence for favoring the B3LYP values of f'.[4]

However, the foregoing argument is flawed because it ignores an unsatisfactory aspect of the whole scaling procedure, namely, that the scale factors involved are in themselves composite, compensating not only for deficiencies in the QC harmonic force field but also for the presence of anharmonicity in the observed frequencies utilized in the scaling. Such anharmonicity has always been recognized to be high in the case of X−H stretching frequencies, but little attention has been paid by practitioners of scaling to the possibility that anharmonicity might vary significantly according to the type of νCH mode, independently

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of any localized effect such as Fermi resonance. The consequence of such a variation would then be the need for *differing* scale factors for the symmetric and antisymmetric stretches of a given type of C−H bond in a CH_2 or CH_3 group. (Attention has previously been drawn to the need for differing scale factors for different types of C−H bond).[5]

Evidence for a systematic variation of the anharmonicity in different types of CH stretching motions should preferably come from molecules where either FR in the νCH region has been accurately assessed or where FR apparently does not exist. In the former class are the methyl halides, where small variations in anharmonicity have been discerned,[6] and ethylene.[7] In the latter class, only methane[8] and dichloromethane[9] are known to us as systems where FR is apparently negligible in the region of the fundamental bands. For dichloromethane, harmonic frequencies have not yet been published, although some anharmonicity constants are available.[9]

Our new studies of the spectra of DFCP appear to show that here also is a system in which there is little evidence for a significant degree of FR in either the νCH or νCD regions of the spectra of the various isotopomers.[1] Weak bands additional to and in close proximity to the fundamentals are seen only occasionally, for example, in the liquid-phase Raman spectra, and these additional bands appear not to arise from the binary levels involving the CH bending modes, which might be expected to be involved in FR.

While a full *experimental* determination of harmonic frequencies is currently out of the question for the type of molecule represented by DFCP, the increasing availability of QC programs that permit calculation of both harmonic and anharmonic vibration frequencies suggests that a theoretical approach is timely. We attempt such an approach in this paper.

There is a further source of dissatisfaction with the current conventional approach to the scaling of harmonic force fields to anharmonic frequencies, particularly where C−H bonds are involved. This deficiency is the inability of the calculation to reproduce at the same time both νCH and νCD frequencies due to the very different effects of anharmonicity on levels spaced far apart in the same potential well. In our previous studies, our ad hoc remedy has been to multiply νCD frequencies, which have been derived from a force field scaled to observed νCH values, by a fudge factor of 1.011 before comparing calculated with observed values. This factor compensates for the smaller effect of anharmonicity on νCD frequencies.[10–12] Panchenko has recommended a similar procedure.[13] Such an approach obviously needs to be tested by a deeper analysis.

Apart from these issues, which relate specifically to the νCH and νCD regions of the spectrum, there is also a wider interest in studying the variations in the scale factor for different types of motion within the molecule. These differences are found whenever close attention is given to scaling to observed anharmonic data. They may arise either from the influence of anharmonicity or from defects in the harmonic force field, or from both of these together. Scaling of the QC-based quadratic force field to observed frequencies that have been corrected for anharmonicity should permit an exploration of the defects inherent in the QC harmonic force field. There is an additional interest in carrying out such a scaling in seeing whether it yields significantly different values of the two force-field-based quantities employed in the process of obtaining the experimental equilibrium geometries of DFCP in ref 1, namely, the harmonic contributions to the alpha constants and the centrifugal distortion constants for the isotopomers involved.

2. Theoretical Section

MP2 and B3LYP calculations were performed using the program Gaussian 03 (G03).[14] Two types of basis set were employed, the Pople-type 6-311++G** and the Dunning correlation-consistent set cc-pVTZ.[15,16] For convenience in the tables below, the following abbreviations are used: B3LYP/6-311++G** ("dtz+"), B3LYP/cc-pVTZ ("dcct"), MP2/6-311++G** ("mtz+"), and MP2/cc-pVTZ ("mcct"). Some B3LYP calculations were also carried out with the aug-cc-pVTZ basis set, but results were so similar to those from the cc-pVTZ set that they are not reported here. Convergence in the prior geometry optimizations was controlled by the "tight" option. For the density functional calculations, a grid of 99 shells, each containing 302 points, was employed, as in previous work from our laboratories.[10,17] Calculations were performed on a Beowulf computation cluster at Oberlin College.

For the calculation of harmonic force constants on a symmetry coordinate basis and subsequent scaling, the G03 output of Cartesian-based force constants was input into the program ASYM40.[18] Such calculations were performed first using observed fundamental anharmonic frequencies, corrected where appropriate for FR, and second on the same frequencies to which were added the harmonic/anharmonic frequency differences $\omega_i - \nu_i = \Delta_i = -2x_{ii} - 1/2 \sum x_{ij}$, as yielded by G03. The resulting data are termed ω_{obsd} in the tables below, but it must be recognized that the anharmonic correction Δ_i incorporated is purely that from an unscaled QC calculation. In such calculations, each x_{ii} or x_{ij} constant involves a series of terms, each of which involves a different cubic or quartic force constant ϕ_{ijk} or ϕ_{ijkl}, the former multiplied by a function involving several frequencies ω_i as required by second-order perturbation theory.[19]

In a more satisfactory approach, applied to the estimation of ω_{obsd} values in benzene, Mani et al. redetermined each x_{ii} or x_{ij} by replacing ω_{QC} values by ω_{obsd} in an iteration process until no further change in x_{ii} or x_{ij} appeared.[20] (Although the harmonic force constants were adjusted, the anharmonic (cubic and quartic) force constants retained their QC values in this process). This procedure required software unavailable to us, and we have had to be content with the cruder procedure described above.

During the course of this work, two weaknesses in the current G03 code were encountered. The first of these involved the entire vibration−rotation package and occurred when the initial geometry optimization gave a Cartesian coordinate system different from the principal axis system (PAS) for the molecule or isotopomer concerned. In the present study, this deficiency affected the d_2 isotopomer and the two 2-$^{13}C_1$ isotopomers used in the determination of the semi-experimental structure. The remedy began by taking the Cartesian coordinates output in the energy optimization in G03 and transforming these coordinates into the PAS with an auxiliary program. These PAS Cartesian coordinates were then used in the Zmat input to G03 with the same model and basis set and the keyword "NoSymm" that tells G03 to preserve the input coordinate system. Negligible changes occur in the reoptimization, and the Cartesian coordinates supplied to the vibration−rotation package remain in the PAS. The preservation of the coordinates in the PAS can be confirmed by checking for a diagonal transformation matrix for the principal moments of inertia, which appears after the vibration frequency output. Coordinates in the PAS are essential for computing correct centrifugal distortion constants, vibration−rotation alpha constants, and anharmonic corrections. This deficiency in G03 did not harm our work on the semi-experimental structure of DFCP because the alphas were computed with other programs.[1] The deficiency did cause small errors in the

TABLE 1: QC Harmonic Frequencies and Estimations of "Experimental" Harmonic Frequencies (cm^{-1}) from QC-Based Anharmonicity Corrections in 1,1-Difluorocyclopropane-d_0

mode		ν_{obs}^{a}	ω_{QC}^{b}				Δ_{QC}^{c}				ω_{obs}^{d}			
			dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct
A$_1$	ν_1	3038	3137.1	3141.9	3194.0	3201.1	120.1	120.3	117.0	119.1	3158.1	3158.3	3155.0	3157.1
	ν_2	1488^e	1512.4	1514.9	1550.8	1546.4	57.8^e	56.5^e	56.9^e	**26.8**	1545.8	1544.5	1544.9	1514.8
	ν_3	1351	1364.5	1370.1	1400.3	1398.2	33.5	34.4	35.4	36.2	1384.5	1385.4	1386.4	1387.2
	ν_4	1007	1032.1	1032.9	1050.1	1031.8	28.1	27.1	28.3	29.1	1035.1	1034.1	1035.3	1036.1
	ν_5	952	957.2	967.3	981.4	991.7	27.7	26.9	29.5	28.5	979.7	978.9	981.5	980.5
	ν_6	702^e	703.3	711.3	721.5	730.9	16.7^e	13.3	14.3	14.9	718.7	715.3	716.3	716.9
	ν_7	468	461.8	467.4	470.9	475.8	3.9	4.4	3.5	4.1	471.9	472.4	471.5	472.1
A$_2$	ν_8	3114	3224.7	3226.9	3296.5	3302.1	146.1	146.0	143.4	142.4	3260.1	3260.0	3257.4	3256.4
	ν_9	1153	1174.7	1180.5	1194.3	1190.1	32.7	32.2	31.6	31.0	1185.7	1185.2	1184.6	1184.0
	ν_{10}	882^f	894.4	892.2	908.5	891.3	14.0	21.4^e	14.3	20.3	896.0	903.4	896.3	902.3
	ν_{11}	335	332.6	333.4	344.4	339.0	5.4	6.3	2.7	2.8	340.4	341.3	337.7	337.8
B$_1$	ν_{12}	3035	3136.2	3141.1	3191.7	3199.1	121.3	121.3	119.1	119.9	3156.3	3156.3	3154.1	3154.9
	ν_{13}	1409	1441.9	1445.8	1462.2	1454.2	38.1	39.1	37.7	40.0	1447.1	1448.1	1446.7	1449.0
	ν_{14}	1075^e	1095.0	1095.1	1120.6	1110.5	35.8^e	34.4^e	37.2^e	37.6^e	1110.8	1109.4	1112.2	1112.6
	ν_{15}	1032	1047.0	1048.2	1063.1	1054.8	24.7	25.8	28.1	26.3	1056.7	1057.8	1060.1	1058.3
	ν_{16}	534	527.1	534.3	547.6	552.4	5.6	6.5	6.2	6.8	539.6	540.5	540.2	540.8
B$_2$	ν_{17}	3120	3235.8	3238.1	3307.0	3312.1	145.1	144.9	143.0	141.9	3265.1	3264.9	3263.0	3261.9
	ν_{18}	1283	1263.3	1283.9	1307.1	1328.2	29.9	31.1	32.1	33.5	1312.9	1314.1	1315.1	1316.5
	ν_{19}	935	926.8	937.0	960.3	963.4	21.0	20.7	22.3	22.0	956.0	955.7	957.3	957.0
	ν_{20}	750	757.0	760.1	770.5	763.2	9.9	8.6	8.2	5.8	759.9	758.6	758.2	755.8
	ν_{21}	350	347.5	349.9	349.6	350.9	−2.1	−1.1	−2.6	−1.1	347.9	348.9	347.4	348.9

[a] Observed frequency from ref 1. [b] Harmonic frequency (ω_{QC}) from B3LYP/6-311++G** (dtz+), B3LYP/cc-pVTZ (dcct), MP2/6-311++G** (mtz+), and MP2/cc-pVTZ (mcct) calculations. [c] $\Delta = (\omega - \nu)_{QC}$. Apparently anomalous value in bold. [d] $\omega_{obs} = \nu_{obs} + \Delta_{QC}$. [e] Fermi resonance correction applied. [f] Estimate from dtz+ force field scaled to observed frequencies.

TABLE 2: QC Harmonic Frequencies and Estimations of "Experimental" Harmonic Frequencies (cm^{-1}) from QC-Based Anharmonicity Corrections in 1,1-Difluorocyclopropane-d_4

sym.	mode	ν_{obs}^{a}	ω_{QC}^{b}				Δ_{QC}^{c}				ω_{obs}^{d}			
			dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct
A$_1$	ν_1	2247	2285.2	2287.9	2328.6	2333.5	56.0	55.5	51.8	55.0	2303.0	2302.5	2298.8	2302.0
	ν_2	1428	1430.7	1436.2	1479.9	1482.2	39.8	40.2	41.1	41.2	1467.8	1468.2	1469.1	1469.2
	ν_3	1066^e	1084.4	1090.7	1106.1	1106.7	32.9^e	33.4^e	35.0^e	**22.3**^{e}	1098.9	1099.4	1101.0	1088.3
	ν_4	879	893.6	899.4	910.8	913.1	24.0^e	23.8^e	24.4^e	24.8	903.0	902.8	903.4	903.8
	ν_5	794	805.3	810.7	818.8	814.6	16.9	17.1	18.4	19.6	810.9	811.1	812.4	813.6
	ν_6	658	657.5	662.1	675.7	678.1	10.4	10.3	11.3	10.6	668.4	668.3	669.3	668.6
	ν_7	454	449.6	454.4	459.0	463.1	4.3	4.8	4.0	4.6	458.3	458.8	458.0	458.6
A$_2$	ν_8	2351	2409.6	2411.2	2463.3	2467.7	78.5	78.1	76.9	77.1	2429.5	2429.1	2427.9	2428.1
	ν_9	911	919.8	924.1	933.4	929.0	17.5	17.5	17.8	17.5	928.5	928.5	928.8	928.5
	ν_{10}	653	671.6	671.1	683.8	673.8	11.7	12.0	12.4	12.2	664.7	665.0	665.4	665.2
	ν_{11}	287	285.8	286.2	296.1	290.6	3.2	4.0	2.1	2.2	290.2	291.0	289.1	289.2
B$_1$	ν_{12}	2228	2271.2	2274.5	2311.3	2316.6	63.1	62.1	68.3	61.5	2291.1	2290.1	2288.3	2289.5
	ν_{13}	1091^e	1104.0	1102.5	1131.7	1122.5	27.2	26.5	28.5	28.5	1118.2	1117.5	1119.5	1119.5
	ν_{14}	1013	1020.8	1022.5	1039.1	1034.8	16.4	17.8	15.4	17.1	1029.4	1030.8	1028.4	1030.1
	ν_{15}	858	871.6	877.3	879.9	874.7	17..6	17.7	20.7	19.4	875.6	875.7	878.7	877.4
	ν_{16}	484	479.0	484.2	497.8	500.1	5.1	5.8	5.8	6.2	489.1	489.8	489.8	490.2
B$_2$	ν_{17}	2353	2410.5	2412.1	2464.3	2468.1	80.3	79.9	79.1	78.4	2433.3	2432.9	2432.1	2431.4
	ν_{18}	1239	1201.4	1228.8	1253.1	1282.8	31.6^e	26.0	26.0	28.0	1270.6	1265.0	1265.0	1267.0
	ν_{19}	787	783.6	788.4	805.7	804.2	13.3	13.1	13.8	13.6	800.3	800.1	800.8	800.6
	ν_{20}	538	540.6	542.8	550.1	545.1	5.8	5.3	5.1	4.0	543.8	543.3	543.1	542.0
	ν_{21}	310	308.6	310.4	310.4	310.8	−0.6	0.3	−1.0	0.2	309.4	310.3	309.4	310.2

[a] Observed frequency from ref 1. [b] Harmonic frequency (ω_{QC}) from B3LYP/6-311++G** (dtz+), B3LYP/cc-pVTZ (dcct), MP2/6-311++G** (mtz+), and MP2/cc-pVTZ (mcct) calculations. [c] $\Delta = (\omega - \nu)_{QC}$. Apparently anomalous value in bold. [d] $\omega_{obs} = \nu_{obs} + \Delta_{QC}$. [e] Fermi resonance correction applied.

anharmonic constants for the d_2 species, which were used in assessing assignments of combination tones.

The second complication was encountered in the calculation, in the anharmonic option, of the values of x_{ij} from the cubic and quartic potential force constants by the second-order perturbation theory referred to above. Occasional major anomalies appeared in the resulting values of x_{ii} or x_{ij} and in the anharmonicity corrections Δ, which are derived from x_{ii} or x_{ij}. These anomalies were traced to an inadequate criterion in the standard code for recognizing the presence of FR. Where such a resonance occurs, associated with a particular cubic force constant ϕ_{ijk}, the corresponding second-order perturbation term in certain x_{ii} or x_{ij} tends to become infinite, leading to a ridiculous value of the x_{ij} concerned. Normal practice is to remove this term and treat the interaction separately by first-order theory. G03 carries out this correct procedure under certain circumstances. However, the default criteria used in the code for the recognition of FR are (1) that the two harmonic levels

TABLE 3: QC Harmonic Frequencies and Estimations of "Experimental" Harmonic Frequencies (cm^{-1}) from QC-Based Anharmonicity Corrections in 1,1-Difluorocyclopropane-d_2

mode		ν_{obs}[a]	ω_{QC}[b]				Δ_{QC}[c]				ω_{obs}[d]			
			dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct
A′	ν_1	3035	3136.7	3141.5	3192.7	3200.1	119.9	119.9	118.6	119.0	3154.9	3154.9	3153.6	3154.0
	ν_2	2236	2278.2	2281.2	2320.0	2325.1	59.8	59.6	56.8	59.4	2294.8	2294.6	2291.8	2294.4
	ν_3	1468	1489.7	1492.7	1526.8	1523.5	**11.9**	43.3	43.4	44.6	**1479.9**	1511.3	1511.4	1512.6
	ν_4	1370	1385.1	1390.5	1419.7	1416.9	33.3	32.3	34.4	34.7	1403.3	1402.3	1404.4	1404.7
	ν_5	1088	1099.9	1099.7	1127.5	1119.5	26.8	26.8	29.3	29.4	1114.8	1114.8	1117.4	1117.4
	ν_6	1047	1063.9	1067.4	1083.6	1079.1	27.1[e]	28.2[e]	29.3[e]	**20.9**	1074.1[e]	1075.2	1076.3[e]	**1067.9**
	ν_7	1019	1036.0	1038.1	1053.5	1043.9	25.3	26.5	27.8[e]	28.3[e]	1044.3	1045.5	1046.8[e]	1047.3
	ν_8	906	919.8	926.8	938.8	943.4	25.0	27.2[e]	25.5	27.4[e]	931.0	933.2	931.5	933.4
	ν_9	820	833.2	837.9	845.2	838.7	16.8	16.8	18.9	19.3	836.8	836.8	838.9	839.3
	ν_{10}	687	685.8	692.4	704.2	711.1	12.5	12.7	13.5	12.8	699.5	699.7	700.5	699.8
	ν_{11}	509	503.1	509.1	521.8	525.3	5.3	5.9	5.9	6.3	514.3	514.9	514.9	515.3
	ν_{12}	459	453.5	458.5	463.2	467.4	4.0	4.4	3.8	4.4	463.0	463.4	462.8	463.4
A″	ν_{13}	3115	3230.3	3232.5	3301.7	3307.1	144.9	144.2	143.1	142.0	3259.9	3259.2	3258.1	3257.0
	ν_{14}	2357	2410.2	2411.9	2464.0	2468.1	80.5	80.8	79.2	78.5	2437.5	2437.8	2436.2	2435.5
	ν_{15}	1262	1235.4	1258.6	1282.1	1306.7	29.8	32.4[e]	28.6	30.7	1291.8	1294.5	1290.6	1292.7
	ν_{16}	1061[f]	1071.4	1077.2	1089.9	1086.0	23.8	24.1	25.7	25.1	1084.8	1087.0	1086.7	1086.1
	ν_{17}	917	915.8	921.6	942.4	938.3	20.5	19.9	20.4	19.9	937.5	936.2	937.4	936.9
	ν_{18}	720	725.1	725.9	739.9	730.9	10.5	11.0	12.8	12.5	730.5	732.2	732.8	732.5
	ν_{19}	620	625.1	627.5	636.7	631.1	6.3	5.4	6.5	5.1	626.3	626.7	626.5	625.1
	ν_{20}	332	330.1	331.9	334.0	333.6	−0.7	−0.5	−0.8	0.0	331.3	332.2	331.2	332.0
	ν_{21}	301	300.7	301.3	310.1	305.7	1.5	2.4	1.4	1.9	302.5	305.0	302.4	302.9

[a] Observed frequency from ref 1. [b] Harmonic frequency (ω_{QC}) from B3LYP/6-311++G** (dtz+), B3LYP/cc-pVTZ (dcct), MP2/6-311++G** (mtz+), and MP2/cc-pVTZ (mcct) calculations. [c] $\Delta = (\omega - \nu)_{QC}$. Apparently anomalous values in bold. [d] $\omega_{obs} = \nu_{obs} + \Delta_{QC}$. [e] Fermi resonance correction applied. [f] Liquid-phase value.

that may interact are found to lie within 10 cm^{-1} of each other and (2) that the magnitude of the cubic force constant concerned is ≥10 cm^{-1}. The first condition excludes nearly every FR familiar to experimentalists working in the field of small- to medium-sized molecules. A more realistic procedure has been suggested by Martin et al.[7] [In later work in this laboratory, an obscure keyword was discovered which enables criterion (1) to be relaxed.]

Analysis of these anomalous G03 results was greatly assisted by a Fortran program that outputs the contributions of individual terms in the second-order expressions for x_{ii} or x_{ij}, using as input the G03 output of cubic and quartic potential constants and harmonic frequencies.

In concluding this section, we note a limitation of the program ASYM40 through which scaling of the QC-based force fields is achieved. This program utilizes the Pulay procedure whereby each off-diagonal symmetry force constant is scaled by the geometric mean of the scale factors for the corresponding two diagonal force constants.[2] Despite theoretical support for such a procedure,[21] experimental evidence indicates its invalidity in certain cases. Thus, MP2 and B3LYP values of the νCH/νCH valence interaction force constant f' differ by a factor of two or more,[4] where only a variation on the order of 10% can result from scaling to the mean of the factors for the diagonal CH stretching force constants. In butadiene, there is evidence for a similar variation in the interaction constant between the stretchings of the two double bonds.[17] Other cases have been noted earlier.[22]

3.Results

3.1. Anharmonicity Corrections Δ. Tables 1−3 show the observed fundamental frequencies, ν_{obsd}, harmonic values, ω_{QC}, anharmonicity corrections, Δ, and the resulting estimates of $\omega_{obsd} = \nu_{obsd} + \Delta$ for the d_0, d_4, and d_2 isotopomers. For the fully symmetric d_0 and d_4 species, the *a* principal rotation axis coincides with the symmetry axis, and the *c* principal rotation axis lies in the plane of the ring, as shown in Figure 1. For the d_2 species, the orientation of the principal rotation axes are similar, but the symmetry axis is absent. The B_1 symmetry species are symmetric with respect to the plane of the cyclopropane ring.

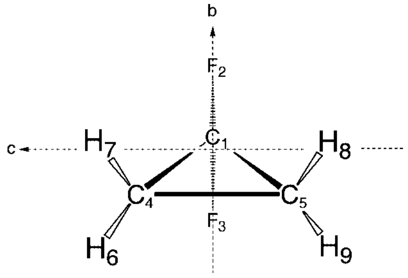

Figure 1. Schematic of 1,1-difluorocyclopropane. Principal rotation axes *b* and *c* are shown; the *a* rotation axis is the twofold symmetry axis lying in the plane of the ring.

Examining the values of Δ, we see a general agreement between the two models, each with the two basis sets, with, however, several exceptions. The notable ones, identified in bold, are for ω_2 (d_0, mcct), ω_3 (d_4, mcct), ω_3 (d_2, dtz+), and ω_6 (d_2, mcct). All of these are associated either with a failure to identify a FR or with an inappropriate handling of such a resonance. The corresponding ω_{obsd} values were omitted in the scaling exercise as were values based on ν_{10} (d_0), which was not observed, and ν_{16} (d_2), which was only seen in the liquid phase. The variation in Δ seen for ω_{10} (d_0) could be a genuine effect of basis set.[23] The Δ_3 for d_2 from the dtz+ model provides a striking example of the limitations of the default options in G03; Δ_3 is heavily influenced by the values of $x_{3,7}$ and $x_{3,12}$, to which the term in $\phi_{3,7,12}$ makes very large contributions. The ω_3 calculated at 1489.71 and $\omega_7 + \omega_{12}$ calculated at 1489.54 cm^{-1} are within 0.17 cm^{-1} of each other, but a FR between the two levels was not recognized by G03 since the value of $\phi_{3,7,12}$ is only 6.4 cm^{-1}.

The most notable feature of these QC values of Δ is the consistent difference between Δ values for the symmetric (A_1

TABLE 4: Symmetry Coordinates for 1,1-Difluorocyclopropane

type of motion	symmetry class				coordinate before normalization[a]
	A_1	B_1	A_2	B_2	
ν_sCH_2	1	8			$(rC_4H_6 + rC_4H_7) \pm (rC_5H_8 + rC_5H_9)$
$\nu_{as}CH_2$			13	17	$(rC_4H_6 - rC_4H_7) \pm (rC_5H_8 - rC_5H_9)$
δ_sCH_2	2	9			$\angle H_6C_4H_7 \pm \angle H_8C_5H_9$
wCH_2	3	10			$\{\angle H_6C_4H_1 - \angle H_6C_4C_5 + \angle H_7C_4H_1 - \angle H_7C_4C_5\} \pm \{\angle H_8C_5H_1 - \angle H_8C_5C_4 + \angle H_9C_5H_1 - \angle H_9C_5C_4\}$
τCH_2			14	18	$\{\angle H_6C_4H_1 - \angle H_6C_4C_5 - \angle H_7C_4H_1 + \angle H_7C_4C_5\} \pm \{\angle H_8C_5H_1 - \angle H_8C_5C_4 - \angle H_9C_5H_1 + \angle H_9C_5C_4\}$
ρCH_2			15	19	$\{\angle H_6C_4H_1 + \angle H_6C_4C_5 - \angle H_7C_4H_1 - \angle H_7C_4C_5\} \pm \{\angle H_8C_5H_1 + \angle H_8C_5C_4 - \angle H_9C_5H_1 - \angle H_9C_5C_4\}$
ν_sCF_2	4				$rC_1F_2 + rC_1F_3$
$\nu_{as}CF_2$				20	$rC_1F_2 - rC_1F_3$
δ_sCF_2	5				$\angle F_2C_1F_3$
wCF_2		11			$\angle F_2C_1C_4 - \angle F_2C_1C_5 + \angle F_3C_1C_4 - \angle F_3C_1C_5$
τCF_2			16		$\angle F_2C_1C_4 - \angle F_2C_1C_5 - \angle F_3C_1C_4 + \angle F_3C_1C_5$
ρCF_2				21	$\angle F_2C_1C_4 + \angle F_2C_1C_5 - \angle F_3C_1C_4 - \angle F_3C_1C_5$
ν_sCCC[b]	6				$rC_1C_4 + rC_1C_5$
ν_sCC[b]	7				rC_4C_5
$\nu_{as}CCC$[b]		12			$rC_1C_4 - rC_1C_5$

[a] Where ± is shown, + applies to the A_1 and A_2 coordinates, and − applies to the B_1 and B_2 ones. For the d_2 species, appropriate linear combinations of the symmetry coordinates were used. [b] These are not simple valence-type coordinates; some angular distortion of the ring is inevitably involved; see ref 23.

and B_1) and antisymmetric (A_2 and B_2) CH stretches, the latter being more than 20 cm^{-1} larger than the former. The same is true with the CD stretches on the smaller scale, which was expected and found. This difference makes it imperative that, in any scaling of the harmonic force field to ν_{obsd}, two scale factors should be employed for CH stretching, even though only a single type of bond is involved. The origin of these variations in Δ for CH stretches is discussed below.

3.2. Scaling Procedures and Scale Factors. Continuing our policy of assessing the need for scaling in fine detail, we introduced independent scale factors for each type of group motion, as specified in the symmetry coordinates defined in Table 4. Figure 1 shows the numbering of atoms for the definitions of symmetry coordinates. In general, where the group motion gave rise to two symmetry coordinates in different symmetry species, the corresponding scale factors were constrained to be equal. However, there appeared to be evidence for differing scale factors for the symmetric CH_2 deformation in the A_1 and B_1 symmetry species, and the corresponding factors were allowed to differ. As discussed in detail below, scaling of the νCH factors was carried out using only the two νCH values ν_1 and ν_{13} (or ω_1 and ω_{13}) of d_2. To fit these exactly, two scale factors proved necessary. The total number of scale factors determined was then 15. The actual refinement was performed simultaneously on the frequencies of the d_0, d_4, and d_2 isotopomers, for which purpose we merged the A_1 and B_1 symmetry classes to form an A′ block and, similarly, the A_2 and B_2 classes to form an A″ block. The numbering of the symmetry coordinates in Table 4 reflects these mergers. Fortunately, no frequency crossing resulted from these mergers, which could distort the refinement. The values of the scale factors and their averages are listed in Table 5. The likely errors quoted for the factors reflect both the fit and the uncertainties in the data, the latter of which were 1% on all frequencies except for the two νCH or ωCH values of d_2 utilized, where ±1 cm^{-1} was chosen. Results of scaling force constants to ν_{obsd} and ω_{obsd} for the four QC models are reported in Supporting Information Tables S1−S3 for the three isotopomers of DFCP.

Several features of the scale factors in Table 5 merit comment. As might be expected from the normal effects of anharmonicity, the mean scale factor for each model rises upon passing from anharmonic (on ν_{obsd}) to harmonic scaling (on ω_{obsd}). The B3LYP harmonic frequencies need to be raised on average about 1% (Δ2% in force constant gives Δ1% in frequency), whereas the MP2 ones require a reduction of about the same value. The ranges of factors required, as represented by the standard deviations of the mean, diminish slightly for the two B3LYP calculations but by somewhat more for the MP2 models. A significant contribution to the range of B3LYP factors comes from the νCF factor, which is as high as 1.16 in the dtz+ ω refinement. This large factor may be associated with the tendency of the B3LYP model to yield bond lengths longer than MP2 or experimental equilibrium ones.[24] The largest variation in the MP2 factors derives from the small scale factor for the wCF_2-embodying S_{11}. This instance, like the νCF_2 factor for the B3LYP force fields, is plainly a defect of the harmonic force field.

Both models need quite different factors for different types of CH bending motion. The factor for the CH_2 twist, τCH_2, (coordinates S_{14}, S_{18}), is particularly low among the anharmonic set of scale factors but close to the mean in the case of the harmonic ones. The difference between the δ_sCH_2 factors for S_2 and S_9 is just significant in the anharmonic refinements but certainly not so in the harmonic cases.

Also explored was the possibility of differing scale factors for the symmetric and antisymmetric CF stretches, S_4 and S_{20}, in a 16 parameter refinement. That for S_4 in the A_1 species proved to be poorly defined, and the two factors were thereafter constrained equally in our 15 parameter calculation.

It is perhaps surprising to find that the overall quality of the fit to observed data in Tables S1–S3, as given by the sum of the weighted squares of errors, ∑WSE, is significantly better for the scaling to anharmonic frequencies than for that based on ω_{obsd} values, although the difference is small for the mcct calculation. Among the refinements to ν_{obsd}, the dcct calculation has the edge over the rest. A specimen force field (mtz+ model, scaled to ν_{obsd}) is included in the Supporting Information, Table S4.

The νCH factors require separate consideration.

3.3. νCH Scale Factors and Frequency Fit. We first look for evidence that might discriminate between the B3LYP and MP2 values of the interaction force constant f'. A positive value

TABLE 5: Scale Factors[a] for QC Force Fields for 1,1-Difluorocyclopropane, Scaled to Observed (ν_{obsd}) and Harmonically Corrected Observed (ω_{obsd}) Frequencies (cm^{-1})

type of motion	symmetry coordinate	dtz+		dcct		mtz+		mcct	
		ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}
ν_sCH_2	$S_1(a_1)$, $S_8(b_1)$	0.9362(2)	1.0116(3)	0.9333(2)	1.0085(3)	0.9036(2)	0.9757(3)	0.8994(2)	0.9714(2)
$\nu_{as}CH_2$	$S_{13}(a_2)$, $S_{17}(b_2)$	0.9299(2)	1.0185(3)	0.9286(2)	1.0166(3)	0.8901(2)	0.9738(3)	0.8872(2)	0.9699(2)
$\Delta\nu CH_2$		−0.0063(4)	0.0069(6)	−0.0047(4)	0.0081(6)	−0.0135(4)	−0.0019(6)	−0.0122(4)	−0.0015(4)
δ_sCH_2	$S_2(a_1)$	0.9389(61)	1.0048((104)	0.9395(59)	1.0116(95)	0.9126(63)	0.9843(90)	0.9299(65)	1.0014(129)
δ_sCH_2	$S_9(b_1)$	0.9595(47)	1.0022(78)	0.9552(46)	1.0003(72)	0.9352(50)	0.9768(69)	0.9463(51)	0.9926(59)
$\Delta\delta_sCH_2$		0.0194(108)	−0.0026(182)	0.0157(105)	−0.0044(167)	0.0226(113)	−0.0075(159)	0.0164(116)	0.0088(188)
wCH_2	$S_3(a_1)$, $S_{10}(b_1)$	0.9502(30)	0.9966(51)	0.9460(30)	0.9929(47)	0.9339(33)	0.9846(45)	0.9606(35)	1.0129(40)
τCH_2	$S_{14}(a_2)$, $S_{18}(b_2)$	0.9141(84)	0.9683(143)	0.9225(84)	0.9882(130)	0.8881(90)	0.9642(123)	0.9158(93)	0.9932(101)
ρCH_2	$S_{15}(a_2)$, $S_{19}(b_2)$	1.0235(86)	1.0346(138)	1.0078(83)	1.0074(117)	0.9881(90)	0.9808(109)	0.9992(91)	0.9872(86)
νCF_2	$S_4(a_1)$, $S_{20}(b_2)$	1.0977(58)	1.1625(96)	1.0377(53)	1.0924(84)	0.9846(56)	1.0328(78)	0.9256(53)	0.9745(62)
δ_sCF_2	$S_5(a_1)$	1.0417(52)	1.0489(82)	1.0118(48)	1.0219(71)	1.0004(53)	1.0061(68)	0.9748(51)	0.9849(55)
wCF_2	$S_{11}(b_1)$	1.0538(71)	1.0530(104)	1.0100(64)	1.0163(91)	0.9643(66)	0.9674(81)	0.9328(63)	0.9393(65)
τCF_2	$S_{16}(a_2)$	1.0039(47)	1.0307(77)	1.0033(46)	1.0390(72)	0.9301(46)	0.9471(63)	0.9687(50)	0.9890(55)
ρCF_2	$S_{21}(b_2)$	1.0316(49)	1.0094(75)	1.0138(47)	0.9958(67)	1.0213(52)	0.9954(65)	1.00890(53)	0.9912(54)
ν_sCCC	$S_6(a_1)^b$	0.9595(87)	1.0123(159)	0.9725(85)	1.0236(135)	0.9042(86)	0.9550(121)	0.9230(88)	0.9673(115)
$\nu_{as}CCC$	$S_{12}(b_1)^b$	0.9719(73)	1.0414(118)	0.9902(72)	1.0556(111)	0.9196(77)	0.9871(103)	0.9438(79)	1.0104(89)
νCC	$S_7(a_1)^b$	0.9420(64)	0.9851(107)	0.9354(60)	0.9787(94)	0.9264(62)	0.9755(86)	0.9184(62)	0.9678(70)
ΣWSE^c		3.38	8.29	3.16	7.02	3.89	6.77	3.96	4.22
mean[d]		0.9812	1.0272	0.9706	1.0169	0.9377	0.9818	0.9392	0.9839
σ_d^e		0.0580	0.0505	0.0406	0.0306	0.0419	0.0213	0.0361	0.0179

[a] Dispersions in parentheses are based on 1% uncertainties in all frequencies utilized except for νCH_2, where ± 1 cm^{-1} was assumed for the two modes in d_2. [b] These ring stretching coordinates involve some angle bending; see ref 23. [c] Sum of weighted squares of frequency errors ε = obsd − calc. [d] Mean scale factor. [e] Standard deviation of mean.

of this constant reduces the $\nu_{as}CH_2/\nu_sCH_2$ splitting, which is primarily dictated by the kinetic energy terms in the *G* matrix. Table 6 shows that substantial differences between MP2 and B3LYP values of f' can be found for the various bonds that involve a common carbon atom (f_α'), although they are much less marked where the CF stretch is involved. The effect is to make the MP2-based $\nu_{as}CH_2/\nu_sCH_2$ splittings larger than those from a B3LYP calculation.

The first procedure, whose results are seen in part A of Table 7, is one which we have adopted in many molecules over past decades. This procedure is to refine a single scale factor to the observed antisymmetric stretching frequency or frequencies because the latter ones have been considered to be those least affected by FR. For DFCP, we use a single datum, the value of ν_{13} or ω_{13} for the d_2 isotopomer. The corresponding fit value ε = obsd − calc = 0.0 cm^{-1} is enclosed in parentheses to identify its use for this purpose. (The total number of scale factors of all kinds refined was then 14, in contrast to the 15 listed in Table 5.) The accompanying predicted νCD_2 frequencies were then multiplied by 1.011 before listing the values of ε.

The ε_ν values for the symmetric CH_2 modes are seen to lie in the range of 8−12 cm^{-1} for the two B3LYP calculations but are much larger, 21−25 cm^{-1}, for the MP2 models. The lower MP2 ν_sCH_2 calculated value, indicated by the larger ε, would then imply that the observed ν_sCH_2 band had been displaced upwards by a significant FR. However, there is very little evidence to support the presence of such a FR affecting any of the symmetric CH_2 stretches in DFCP. This type of analysis therefore favors the larger B3LYP value of f', which produces higher values of ν_sCH_2 and thus smaller ε's.

In marked contrast to these results, obtained by refining to ν_{obs}, are those where, instead, the harmonic frequencies are employed. With the latter, reproduction of the ω_sCH_2 values is good using the MP2 model, whereas the B3LYP results are markedly worse. This result strongly favors the MP2 values of f'. The apparent advantage derived from the B3LYP force field when applied to ν values is now seen to be due to neglect of the differences in anharmonicity of the symmetric and antisymmetric CH stretching modes.

Part B of Table 7 expresses this truth in a different way, when taken in conjunction with the scale factors for this treatment, which are shown in Table 5. Refining two CH stretching scale factors to fit exactly the two CH stretches of d_2, we find a roughly comparable quality of fit to the other CH stretches ν_{obsd} and ω_{obsd} from both MP2 and B3LYP models. Reference to Table 6, however, shows that the MP2 scale factors for ω_{obsd} refinements are rather closer to each other, as might be expected for a pair of identical bonds, than those from the B3LYP models. The opposite is true for the ν_{obsd} results. Such differences are best explained as arising from the difference inherent in the f' values, again favoring the MP2 result. A slightly larger value of f' than that for the MP2 ones could give identical scale factors in the ω_{obsd} treatments.

Turning to the prediction of $\nu/\omega CD$ values, we see that the factor of 1.011 gives predictions of $\nu_{as}CD_2$ which are comparable in precision with those for $\omega_{as}CD_2$. This outcome is not surprising since antisymmetric stretching frequencies were used as the source for this empirical parameter.[10–12] Predictions of ν_sCD_2, however, are rather poor when only one scale factor is employed but somewhat better with two scale factors, particularly with the MP2 model. With two scale factors, a fudge factor of 1.013−1.015 would be needed to give a good fit to observed ν_sCD_2 values.

Overall, the fits obtained from the ω_{obsd} refinements are compatible with the suggestions that the B3LYP and MP2 estimates of CH/CD anharmonicity are on target and that the observed νCD values are little affected by FR.

3.4. Frequency Fit: Other Modes. Unobserved Frequencies. The complete set of frequency fits ε = obsd − calc with scaled force fields is given in the Supporting Information Tables S1, S2, and S3 for the d_0, d_4, and d_2 isotopomers, respectively. However, as examples of the fits obtained, we quote in Tables 8−10 the results from the mtz+ model for the three isotopomers for both ν_{obsd} and ω_{obsd} refinements. Included in these tables

TABLE 6: Unscaled QC Values of Valence Interaction Force Constants in 1,1-Difluorocyclopropane (aJ Å^{-2})

interaction type	bond pairs[a]	dtz+	dcct	mtz+	mcct
gem	CH/CH	0.0200	0.0251	−0.0026	0.0018
	CH/C_1C_4	0.0372	0.0414	0.0153	0.0171
	CH/C_4C_5	0.0618	0.0659	0.0392	0.0384
	CF/CF	0.7269	0.7436	0.6715	0.6930
	CF/C_1C_4	0.3813	0.3931	0.3567	0.3734
β	CH_a/CH_a	0.0068	0.0071	0.0049	0.0046
	CH_a/CH_b	−0.0135	−0.0132	−0.0135	−0.0134
	$>CH_a/CF_a$	0.0103	0.0115	0.0050	0.0066
	CH_a/CF_b	−0.0023	−0.0005	−0.0035	−0.0022
	CF/C_4C_5	−0.1269	−0.1183	−0.1249	−0.1202

[a] Atoms H_a and F_a are on the same side of the ring plane; H_a and H_b or F_a and F_b are on opposite sides.

TABLE 7: Fit ε = Observed − Calculated of CH and CD Stretching Frequencies (cm^{-1}) for Two Scaling Procedures

A: One CH Stretching Scale Factor Fitted to $\nu/\omega_{as}CH_2$ (ν/ω_{13}) in DFCP-d_2

model	d_0				d_2		d_4				d_2	
	ν_sCH_2		$\nu_{as}CH_2$		ν_sCH_2	$\nu_{as}CH_2$	ν_sCD_2		$\nu_{as}CD_2$		ν_sCD_2	$\nu_{as}CD_2$
	$\varepsilon(\nu_1(a_1))$	$\varepsilon(\nu_{17}(b_1))$	$\varepsilon(\nu_8(a_2))$	$\varepsilon(\nu_{17}(b_2))$	$\varepsilon(\nu_1(a'))$	$\varepsilon(\nu_{13}(a''))$	$\varepsilon(\nu_1(a_1))$	$\varepsilon(\nu_{17}(b_1))$	$\varepsilon(\nu_8(a_2))$	$\varepsilon(\nu_{17}(b_2))$	$\varepsilon(\nu_2(a'))$	$\varepsilon(\nu_{14}(a''))$
dtz+	12.4	10.7	−0.3	4.3	10.2	(0.0)	18.2	13.4	2.6	−0.5	13.2	6.4
dcct	10.1	8.1	−0.3	4.3	7.6	(0.0)	16.9	11.6	0.7	2.7	11.7	6.5
mtz+	24.5	23.9	0.1	3.9	22.7	(0.0)	24.9	23.2	0.3	2.1	21.4	6.0
mcct	22.6	21.7	0.4	3.6	20.6	(0.0)	23.3	21.3	−0.5	2.2	19.7	5.6
	ω_sCH_2		$\omega_{as}CH_2$		ω_sCH_2	$\omega_{as}CH_2$	ω_sCD_2		$\omega_{as}CD_2$		ω_sCD_2	$\omega_{as}CD_2$
	$\varepsilon(\omega_1(a_1))$	$\varepsilon(\omega_{17}(b_1))$	$\varepsilon(\omega_8(a_2))$	$\varepsilon(\omega_{17}(b_2))$	$\varepsilon(\omega_1(a'))$	$\varepsilon(\omega_{13}(a''))$	$\varepsilon(\omega_1(a_1))$	$\varepsilon(\omega_{17}(b_1))$	$\varepsilon(\omega_8(a_2))$	$\varepsilon(\omega_{17}(b_2))$	$\varepsilon(\omega_2(a'))$	$\varepsilon(\omega_{14}(a''))$
dtz+	−7.8	−8.8	5.8	−0.4	−10.6	(0/0)	−2.6	−1.2	−2.3	0.7	−4.2	5.1
dcct	−9.5	−10.8	6.5	0.0	−12.5	(0.0)	−3.9	−3.4	−1.9	0.9	−5.5	6.1
mtz+	3.4	4.6	4.5	−0.3	3.1	(0.0)	1.4	7.5	−2.8	0.3	2.6	4.8
mcct	4.5	4.2	4.3	0.0	2.4	(0.0)	4.0	7.6	−2.5	0.6	4.3	4.6

B. Two CH Stretching Scale Factors Fitted Respectively to ν/ω_sCH_2 (ν/ω_1) and $\nu/\omega_{as}CH_2$ (ν/ω_{13}) in DFCP-d_2

model	d_0				d_2		d_4				d_2	
	ν_sCH_2		$\nu_{as}CH_2$		ν_sCH_2	$\nu_{as}CH_2$	ν_sCD_2		$\nu_{as}CD_2$		ν_sCD_2	$\nu_{as}CD_2$
	$\varepsilon(\nu_1(a_1))$	$\epsilon=\varepsilon(\nu_{17}(b_1))$	$\varepsilon(\nu_8(a_2))$	$\varepsilon(\nu_{17}(b_2))$	$\varepsilon(\nu_1(a'))$	$\varepsilon(\nu_{13}(a''))$	$\varepsilon(\nu_1(a_1))$	$\varepsilon(\nu_{17}(b_1))$	$\varepsilon(\nu_8(a_2))$	$\varepsilon(\nu_{17}(b_2))$	$\varepsilon(\nu_2(a'))$	$\varepsilon(\nu_{14}(a''))$
dtz+	2.5	0.5	4.3	−0.3	(0.0)	(0.0)	11.0	6.0	0.5	2.6	5.9	6.4
dcct	2.5	0.5	4.3	−0.3	(0.0)	(0.0)	11.5	6.1	−0.7	2.7	6.2	6.5
mtz+	1.9	1.1	3.9	0.1	(0.0)	(0.0)	8.7	6.7	0.3	2.1	5.1	6.0
mcct	2.0	1.0	3.6	0.4	(0.0)	(0.0)	8.7	6.3	−0.5	2.2	4.9	5.6
	ω_sCH_2		$\omega_{as}CH_2$		ω_sCH_2	$\omega_{as}CH_2$	ω_sCD_2		$\omega_{as}CD_2$		ω_sCD_2	$\omega_{as}CD_2$
	$\varepsilon(\omega_1(a_1))$	$\varepsilon(\omega_{17}(b_1))$	$\varepsilon(\omega_8(a_2))$	$\varepsilon(\omega_{17}(b_2))$	$\varepsilon(\omega_1(a'))$	$\varepsilon(\omega_{13}(a''))$	$\varepsilon(\omega_1(a_1))$	$\varepsilon(\omega_{17}(b_1))$	$\varepsilon(\omega_8(a_2))$	$\varepsilon(\omega_{17}(b_2))$	$\varepsilon(\omega_2(a'))$	$\varepsilon(\omega_{14}(a''))$
dtz+	2.8	1.8	5.8	0.4	(0.0)	(0/0)	4.9	6.5	−2.3	0.7	3.3	5.1
dcct	3.0	1.8	6.5	0.0	(0.0)	(0.0)	4.9	5.6	−1.9	0.9	3.5	6.1
mtz+	0.4	1.5	4.5	−0.3	(0.0)	(0.0)	−0.7	5.3	−2.8	0.3	0.4	4.8
mcct	2.2	1.8	4.3	0.0	(0.0)	(0.0)	2.3	5.8	−2.5	0.6	2.6	4.6

are the potential energy distributions (PED) for both cases. As might be expected, the PEDs show only an occasional variation between the ν_{obsd} and ω_{obsd} refinement results. Two frequency data, except νCH/CD frequencies indicated above, had been omitted from all eight refinements due either to ignorance or to uncertainty in their position. The unobserved fundamental $\nu_{10}(a_2)$ in d_0 is predicted alternatively at 882.0 (dtz+), 878.9 (dcct), 880.3 (mtz+), or 873.8 cm^{-1} (mcct). The $\nu_{16}(a'')$ mode in d_2 was omitted because it was seen in the liquid state only at 1061 cm^{-1}. The refinement values are 1055.3 (dtz+), 1058.3 (dcct), 1054.3 (mtz+), or 1060.2 cm^{-1} (mcct) so that there is no clear evidence for a significant gas/liquid frequency shift.

Finally, in this section, we note that Table S5 in the Supporting Information contains values of ν_{obsd} for the d_1 and d_3 isotopomers as predicted by the scaled dtz+ force field. Such predictions had previously been used to identify likely impurity bands in the d_2 and d_4 spectra.[1]

3.5. Vibration−Rotation Constants (Alphas). Harmonic contributions to the vibration−rotation (alpha) constants had been originally obtained from ASYM40 using the QC force fields scaled to ν_{obsd} only.[1] To test the sensitivity of the results for alphas to the method of calculation, we have now repeated this calculation using both unscaled force fields and those scaled to ω_{obsd}, employing the dcct and mcct models. Table 11 compares the results for the d_0 isotopomer obtained by the three procedures. The differences found are indeed small and are estimated to have a negligible effect on the overall adjustment of ground-state rotational constants to equilibrium values and hence on the subsequent geometry obtained. A curious feature of the results in Table 11 is that the unscaled values of the alphas agree very closely with those from the ω_{obsd} force field for the mcct model, whereas for the dcct model, it is the unscaled and ν_{obsd} values which almost coincide.

TABLE 8: Comparison of Observed and Scaled QC Frequencies (cm^{-1}) from MP2/6-311++G Force Fields in 1,1-Difluorocyclopropane-d_0**

sym.	mode	ν_{obsd}^{a}	ε_ν^{b}	ω_{obsd}^{a}	ε_ω^{b}	PED^c (ν_{obsd})	PED^c (ω_{obsd})
A_1	ν_1	**3038**	1.9	**3155.0**	0.4	$100S_1$	$100S_1$
	ν_2	1488^d	−0.2	1544.9	10.1	$47S_2, 16S_4, 6S_5, 44S_6, 6S_7$	$54S_2, 14S_4, 5S_5, 39S_6, 6S_7$
	ν_3	1351	1.6	1386.4	−5.2	$56S_2, 23S_4, 8S_5, 22S_6$	$49S_2, 25S_4, 8S_5, 27S_6$
	ν_4	1007	−8.1	1035.3	−7.0	$108S_3, 5S_7$	$108S_3, 5S_7$
	ν_5	952	−1.6	981.5	3.8	$31S_4, 5S_6$ $67S_7$	$31S_4, 67S_7$
	ν_6	702^d	0.3	716.3	−2.6	$31S_4, 7S_5, 23S_6, 31S_7$	$31S_4, 6S_5, 24S_6, 31S_7$
	ν_7	468	0.4	471.5	0.6	$79S_5, 10S_6$	$80S_5$
A_2	ν_8	**3114**	3.9	**3257.4**	4.5	$100S_{13}$	$100S_{13}$
	ν_9	1153	2.3	1184.6	8.1	$48S_{14}, 35S_{15}$	$56S_{14}, 29S_{15}$
	ν_{10}	**879.3**^{e}	(0.0)	**896.3**	1.2	$54S_{14}, 53S_{15}$	$46S_{14}, 59S_{15}. 5S_{16}$
	ν_{11}	335	1.6	337.7	1.8	$13S_{14}, 21S_{15}, 105S_{16}$	$13S_{14}, 22S_{15}, 104S_{16}$
B_1	ν_{12}	**3035**	1.1	**3154.1**	1.5	$100S_8$	$100S_8$
	ν_{13}	1409	−5.1	1446.7	1.6	$103S_9$	$103S_9$
	ν_{14}	1075^d	−4.9	1112.2	0.4	$36S_{10}, 11S_{11}, 64S_{12}$	$36S_{10}, 10S_{11}, 65S_{12}$
	ν_{15}	1032	3.4	1060.1	6.4	$64S_{10}, 22S_{11}, 18S_{12}$	$65S_{10}, 21S_{11}, 19S_{12}$
	ν_{16}	534	−0.4	540.2	0.3	$68S_{11}, 21S_{12}$	$71S_{11}, 19S_{12}$
B_2	ν_{17}	**3120**	0.1	**3263.0**	−0.3	$100S_{17}$	$100S_{17}$
	ν_{18}	1283	0.5	1315.1	5.9	$20S_{18}, 11S_{19}, 66S_{20}, 16S_{21}$	$22S_{18}, 10S_{19}, 67S_{20}, 14S_{21}$
	ν_{19}	935	−4.1	957.3	−3.6	$21S_{18}, 22S_{19}, 45S_{20}$	$26S_{18}, 17S_{19}, 44S_{20}$
	ν_{20}	750	−2.0	758.2	−3.0	$45S_{18}, 69S_{19}$	$40S_{18}, 76S_{19}$
	ν_{21}	350	−0.8	347.4	−0.9	$30S_{18}, 109S_{21}$	$28S_{18}, 110S_{21}$
ΣWSE^f			1.73		3.00		

[a] Wavenumbers (cm^{-1}). In bold, data not used in the 15 parameter scale factor refinements to anharmonic (ν_{obsd}) and harmonic (ω_{obsd}) frequencies. [b] $\varepsilon_\nu = \nu_{obsd} - \nu_{calc.}$; $\varepsilon_\omega = \omega_{obsd} - \omega_{calc.}$ [c] Potential energy distribution: diagonal terms ≥ 5%. Large off-diagonal terms are present in several modes. [d] Corrected for Fermi resonance. [e] Value from the mtz+ force field scaled to ν_{obsd}. [f] Sum of weighted squares of errors.

TABLE 9: Comparison of Observed and Scaled QC Frequencies (cm^{-1}) from Scaled MP2/6-311++G Force Fields in 1,1-Difluorocyclopropane-d_4**

sym.	mode	ν_{obs}^{a}	ε_ν^{b}	ω_{obs}	ε_ω^{b}	PED(ν_{mtz+})	PED(ω_{mtz+})
A_1	ν_1	2247	8.7	2298.8	−0.7	$97S_1$	$97S_1$
	ν_2	*1428*	−1.6	*1469.1*	3.3	$5S_2, 34S_4, 13S_5, 64S_6, 5S_7$	$6S_2, 34S_4, 12S_5, 64S_6, 6S_7$
	ν_3	*1066*^{c}	−0.8	*1101.0*	−1.3	$74S_2, 21S_4, 23S_7$	$76S_2, 21S_4, 21S_7$
	ν_4	*879*	1.4	*903.4*	0.1	$19S_2, 14S_3, 9S_4, 56S_7$	$17S_2, 13S_3, 10S_4, 57S_7$
	ν_5	*794*	0.3	*812.4*	−2.7	$6S_2, 75S_3, 19S_4, 13S_6, 7S_7$	$5S_2, 76S_3, 19S_4, 14S_6, 7S_7$
	ν_6	*658*	0.7	*669.3*	−3.4	$19S_3, 18S_4, 13S_5, 12S_6,19S_7$	$19S_3, 18S_4, 12S_5, 12S_6, 19S_7$
	ν_7	*454*	−0.7	*458.0*	−0.5	$73S_5$	$75S_5$
A_2	ν_8	2351	0.3	2427.9	−2.8	$100S_{13}$	$100S_{13}$
	ν_9	*911*	2.8	*928.8*	−8.4	$28S_{14}, 49S_{15}, 8S_{16}$	$34S_{14}, 44S_{15}, 7S_{16}$
	ν_{10}	*653*	−1.2	*665.4*	−6.6	$71S_{14}, 28S_{15}, 6S_{16}$	$66S_{14}, 32S_{15}, 7S_{16}$
	ν_{11}	*287*	−0.3	*289.1*	−0.1	$15S_{14}, 31S_{15}, 98S_{16}$	$15S_{14}, 32S_{15}, 97S_{16}$
B_1	ν_{12}	2228	6.7	2288.3	5.3	$100S_8$	$100S_8$
	ν_{13}	*1091*^{c}	−0.2	*1119.5*	−1.5	$52S_9, 12S_{11}, 59S_{12}$	$48S_9, 11S_{11}, 63S_{12}$
	ν_{14}	*1013*	8.0	*1028.4*	0.8	$50S_9, 17S_{11}, 23S_{12}$	$53S_9, 14S_{11}, 22S_{12}$
	ν_{15}	*858*	5.9	*878.7*	6.6	$90S_{10}, 16S_{11}$	$91S_{10}, 16S_{11}$
	ν_{16}	*484*	−1.0	*489.8*	−1.4	$9S_{10}, 57S_{11}, 20S_{12}$	$8S_{10}, 60S_{11}, 18S_{12}$
B_2	ν_{17}	2353	2.1	2432.1	0.3	$100S_{17}$	$100S_{17}$
	ν_{18}	*1239*	2.0	*1265.0*	1.7	$11S_{18}, 5S_{19}, 87S_{20}, 17S_{21}$	$11S_{18}, 5S_{19}, 88S_{20}, 16S_{21}$
	ν_{19}	*787*	1.0	*800.8*	−1.2	$25S_{18}, 23S_{19}, 24S_{20}$	$29S_{18}, 20S_{19}, 23S_{20}$
	ν_{20}	*538*	−0.3	*543.1*	−0.5	$38S_{18}, 74S_{19}$	$36S_{18}, 77S_{19}$
	ν_{21}	*310*	0.4	*309.4*	0.6	$43S_{18}, 103S_{21}$	$40S_{18}, 105S_{21}$
ΣWSE			1.42	1.44	2.99		

[a] Wavenumbers (cm^{-1}). In italics, values used for scaling the force fields. [b] $\varepsilon_\nu = \nu_{obsd} - \nu_{calc.}$; $\varepsilon_\omega = \omega_{obsd} - \omega_{calc.}$ Calculated values of νCD were premultiplied by 1.011 to offset the differing effects of anharmonicity on νCH and νCD frequencies. [c] Value corrected for Fermi resonance.

Alpha data for all five isotopomers used in the geometry determinations are listed in Table S6 of the Supporting Information. Small differences exist in the alphas computed with the four QC models. At most, the alphas contribute 1% to adjusting the ground-state rotational constants to equilibrium rotational constants. Thus, using alphas from different models makes a negligible change in the geometric parameters in the semi-experimental structure. Furthermore, alphas computed (correctly with PAS coordinates) with G03 without scaling are sufficient for the semi-experimental structure.

3.6. Centrifugal Distortion Constants. Quartic centrifugal distortion constants (CDCs), calculated through ASYM40 from the dcct force field scaled to ν_{obsd}, were employed in ref 1 to improve the accuracy of the ground-state rotational constants for the five isotopomers used in the geometry determinations.[25] These were the d_0, d_0-2-$^{13}C_1$, d_4, d_4-1-$^{13}C_1$, and d_4-2-$^{13}C_1$ species. The original cw microwave spectra had lacked the accuracy to enable experimental values of the CDCs to be determined.[26] In the meantime, fresh FT microwave spectra with an accuracy of about 20 times greater have been obtained, enabling experi-

TABLE 10: Comparison of Observed and Scaled QC Frequencies (cm^{-1}) from Scaled MP2/6-311++G in 1,1-Difluorocyclopropane-2,2-d_2**

sym.	mode	ν_{obs}[a]	ε_{ν}[b]	ω_{obs}[a]	ε_{ω}[b]	PED ($\nu_{\text{mtz+}}$)	PED ($\omega_{\text{mtz+}}$)
A′	ν_1	*3035*	*0.0*	3153.6	0.0	$50S_1, 50S_8$	$50S_1, 50S_8$
	ν_2	2235[c]	5.1	2291.8	0.4	$48S_1, 50S_8$	$48S_1, 50S_8$
	ν_3	*1468*	*−0.9*	1511.4	0.7	$30S_2, 18S_4, 7S_5, 42S_6, 5S_7, 15S_9$	$34S_2, 16S_4, 6S_5, 40S_6, 5S_7, 16S_9$
	ν_4	*1370*	*−2.0*	1404.4	−3.4	$21S_2, 19S_4, 7S_5, 22S_6, 40S_9$	$20S_2, 20S_4, 7S_5, 25S_6, 36S_9$
	ν_5	*1088*	*2.1*	1117.4	−1.2	$20S_2, 21S_9, 6S_{10}, 11S_{11}, 56S_{12}$	$19S_2, 22S_9, 6S_{10}, 10S_{11}, 57S_{12}$
	ν_6	*1047*[d]	*−0.8*	1076.3[d]	−0.3	$17S_2, 11S_3, 11S_4, 7S_7, 16S_9, 24S_{10}, 12S_{12}$	$17S_2, 11S_3, 11S_4, 6S_7, 17S_9, 24S_{10}, 11S_{12}$
	ν_7	*1019*[d]	*0.0*	1046.8[d]	2.3	$5S_2, 31S_3, 11S_7, 31S_{10}, 17S_{11}, 13S_{12}$	$32S_3, 11S_7, 31S_{10}, 15S_{11}, 14S_{12}$
	ν_8	*906*	*−1.7*	931.5	−0.3	$9S_2, 15S_4, 52S_7, 8S_9$	$8S_2, 16S_4, 53S_7, 8S_9$
	ν_9	*820*	*1.2*	838.9	−0.9	$56S_3, 9S_4, 6S_6, 31S_{10}, 6S_{11}$	$56S_3, 9S_4, 6S_6, 32S_{10}, 6S_{11}$
	ν_{10}	*687*	*2.1*	700.5	−0.6	$25S_4, 9S_5, 18S_6. 26S_7$	$25S_4, 8S_5, 19S_6. 26S_7$
	ν_{11}	*509*	*−0.5*	514.9	−0.4	$7S_5, 57S_{11}, 19S_{12}$	$6S_5, 60S_{11}, 17S_{12}$
	ν_{12}	*459*	*0.2*	462.8	0.3	$70S_5, 10S_6$	$72S_5, 10S_6$
A″	ν_{13}	*3115*	0.0	3258.1	0.0	$50S_{13}, 51S_{17}$	$50S_{13}, 51S_{17}$
	ν_{14}	2357	6.0	2436.2	4.8	$50S_{13}, 50S_{17}$	$50S_{13}, 50S_{17}$
	ν_{15}	*1262*	*1.6*	1290.6	3.2	$16S_{18}, 8S_{19}, 75S_{20}, 16S_{21}$	$17S_{18}, 7S_{19}, 76S_{20}, 15S_{21}$
	ν_{16}	1061[e]	6.7	1086.7	11.9	$38S_{14}, 38S_{15}$	$46S_{14}, 31S_5$
	ν_{17}	*917*	*−2.4*	937.4	−0.9	$15S_{14}, 14S_{15}, 17S_{18}, 15S_{19}, 30S_{20}$	$10S_{14}, 19S_{15}, 18S_{18}, 15S_{19}, 28S_{20}$
	ν_{18}	*720*	*2.3*	732.8	2.5	$39S_{14}, 30S_{15}, 5S_{16}, 14S_{19}, 5S_{20}$	$38S_{14}, 32S_{15}, 5S_{16}, 5S_{18}, 9S_{19}, 5S_{20}$
	ν_{19}	*620*	*0.2*	626.5	−2.1	$8S_{14}, 40S_{18}, 60S_{19}$	$6S_{14}, 37S_{18}, 67S_{19}$
	ν_{20}	*332*	*0.5*	331.2	0.3	$15S_{16}, 34S_{18}, 90S_{21}$	$19S_{16}, 31S_{18}, 87S_{21}$
	ν_{21}	*301*	*−1.6*	302.4	−1.7	$14S_{14}, 24S_{15}, 84S_{16}, 15S_{21}$	$13S_{14}, 24S_{15}, 80S_{16}, 19S_{21}$
ΣWSE			0.73		0.79		

[a] In italics, frequency (cm^{-1}) used in scaling the force field. [b] $\varepsilon_\nu = \nu_{\text{obsd}} - \nu_{\text{calc.}}$; $\varepsilon_\omega = \omega_{\text{obsd}} - \omega_{\text{calc}}$. Calculated values of νCD were premultiplied by 1.011 to offset the differing effects of anharmonicity on νCH and νCD frequencies. [c] Revised to 2236 cm^{-1} in the companion paper. [d] Value corrected for Fermi resonance. [e] Liquid-phase value.

TABLE 11: Harmonic Contributions to Alpha Constants for DFCP-d_0 Calculated in Different Ways (in cm^{-1})

	$1/2\alpha_a$		$1/2\alpha_b$		$1/2\alpha_c$	
force field	dcct	mcct	dcct	mcct	dcct	mcct
unscaled	−7.37	−7.17	−6.72	−6.70	−2.29	−2.20
scaled to ω_{obsd}	−7.20	−7.28	−6.61	−6.76	−2.17	−2.25
scaled to ν_{obsd}	−7.40	−7.52	−6.71	−6.86	−2.28	−2.35

mental values of the CDCs for several isotopomers to be determined. Details of this work will appear elsewhere,[27] but here, we quote in Table 12 the new CDC data for DFCP-d_0. Also in this table are the results computed from the force fields for the four models, each force field either unscaled or scaled to ν_{obsd} or ω_{obsd}.

We note first that agreement between the dcct (ν_{obsd}) result and experiment is satisfactory in view of the experimental uncertainties with the mild exception of Δ_K, indicating that revision of the geometry determinations is likely to prove unnecessary. Second, we observe in Table 12 several striking changes with the method of scaling in the predicted CDCs, notably with Δ_K (up to 20%) and δ_K (up to 220%). Since we lack the means of identifying the specific factors within the force field that contribute to the overall value of a particular CDC, we can only look for what we might anticipate, namely, that a general diminution in CDC might accompany a general rise in vibrational frequency, the latter reflecting a stiffening of the molecule. (The other significant component of the CDC calculation, the geometry of the molecule, is the same for all ASYM40 calculations undertaken with a given model.) The effect of stiffness would lead us to expect smaller CDC values from the force fields scaled to ω_{obsd} than from those scaled to ν_{obsd} because of the larger scale factors of the former. This outcome is indeed found for four of the five CDCs but not for Δ_{JK}.

A more consistent picture emerges when we compare CDCs in Table 12 from the unscaled force fields with those scaled to ω_{obsd}. For both B3LYP models, the ω_{obsd} frequencies are generally higher than the unscaled ω_{QC} frequencies, leading to the prediction that CDCs should rise in passing from the ω_{obsd} to the unscaled force field. Conversely, the MP2 ω_{QC} frequencies are consistently higher than the ω_{obsd} frequencies so that MP2-based CDCs should fall upon passing from the ω_{obsd} scaled force field to an unscaled one. Both of these predictions are obeyed throughout.

A smaller effect is expected from the differences between calculated B3LYP and MP2 equilibrium geometries, which lead to rotational constants from MP2 models being slightly larger than those from DFT models. This will tend to make CDCs from MP2 models slightly larger than those from DFT ones. The effect appears to be noticeable in comparing ω_{obsd}-based values, where the influence of differing frequencies is expected to be minimal.

In comparing any of these calculated CDCs with experimental values, it has constantly to be borne in mind that the calculated values refer to the hypothetical equilibrium state whereas the experimental ones refer to the ground state of the molecule. Little is known about the vibrational dependence of CDCs. However, the view has been expressed that differences of up to 10% may be expected between ground-state and equilibrium values.[28] In making such a comparison, it would seem logical to employ the CDCs calculated with the force fields scaled to ω_{obsd} since these are based on the best vibrational description of the equilibrium state that the model concerned can provide. Passing from ν_{obsd} scaling to ω_{obsd} scaling is seen to improve agreement with experiment in two cases, Δ_{JK} and Δ_K, to have little effect on the same comparison for Δ_J and δ_J, but to increase the disagreement over δ_K. For two of the models, dcct and mcct, the disagreement between experimental and ω_{obsd} results for δ_K is beyond the combined error limits of experiment and the arbitrary 10% accorded above to vibrational dependence of the CDCs. Further study will be needed to elucidate this issue.

For experimental work, we note that, with the exception of one value for the mtz+ model without scaling in Table 12, any of the unscaled approximations to the CDCs are sufficiently good to be useful in improving the fit of a limited set of

TABLE 12: Comparison of Experimental and Calculated Centrifugal Distortion Constants for 1,1-Difluorocyclopropane

const.	expt.[a]	dcct[b]			dtz+[b]			mcct[b]			mtz+[b]		
		ν_{obsd}[c]	ω_{obsd}	unsc	ν_{obsd}	ω_{obsd}	unsc	ν_{obsd}	ω_{obsd}	unsc	ν_{obsd}	ω_{obsd}	unsc
δ_J/kHz	0.309(3)	0.312	0.306	0.310	0.308	0.302	0.309	0.321	0.315	0.309	0.316	0.310	0.304
δ_K/kHz	−0.21(1)	−0.187	−0.106	−0.172	−0.209	−0.136	−0.161	−0.185	−0.125	−0.122	−0.219	−0.150	−0.065
Δ_K/kHz	0.70(4)	0.807	0.704	0.736	0.799	0.690	0.781	0.812	0.691	0.643	0.774	0.643	0.70
Δ_{JK}/kHz	1.73(2)	1.60	1.65	1.70	1.55	1.60	1.70	1.64	1.70	1.70	1.59	1.67	1.66
Δ_J/kHz	1.23(1)	1.23	1.19	1.23	1.21	1.17	1.23	1.28	1.24	1.21	1.26	1.21	1.20

[a] From fitting, 33 microwave lines: 26 from new observations from pulsed-jet FT cavity measurements; 7 from cw measurements with reduced weight; ref 26. Watson-type Hamiltonian with asymmetric top reduction and I^r representation. [b] Predictions from ASYM40 with force constants either scaled to ν_{obsd} or ω_{obsd} or unscaled for various QC models. [c] These values and corresponding ones for the other isotopomers were used in ref 1 to refit the ground-state rotational constants for use in the geometry determinations.

TABLE 13: Major Contributions to the Difference in Anharmonicity Corrections Δ_i (cm^{-1}) for the CH Stretches ω_1 and ω_{13} in DFCP-d_2, from the mtz+ Model

$x_{r,s}$ term	contribution to $\Delta_{13} - \Delta_1$
$-2(x_{13,13} - x_{1,1})$	8.64
$-0.5(x_{13,3} - x_{1,3})$	8.37
$-0.5(x_{13,4} - x_{1,4})$	3.36
$-0.5(x_{13,6} - x_{1,6})$	1.50
$-0.5(x_{13,7} - x_{1,7})$	2.30
sum of 5 terms	24.1
total (21 terms)	24.5

rotational transitions to rotational constants. The CDCs computed with G03 (with PAS coordinates) are the same as the unscaled values obtained with ASYM40. In the past, the alternative has been to fit limited rotational data with a rigid rotor approximation, in which all CDCs are set to zero, or with a semi-rigid rotor model, in which the indeterminate CDCs are set to zero. Fits of δ_J and δ_K have often been unacceptable with older microwave and newer high-resolution infrared data. Thus, using predicted values for δ_J and δ_K is a good way to improve the fit of the other rotational constants. Additional examples of satisfactory agreement between observed and calculated (with ASYM40) centrifugal distortion constants are in the recent literature.[29,30]

The predictive value of QC-based CDCs would of course be enhanced if the vibrational dependence of the CDCs could also be estimated. A program to accomplish this, in a manner similar to that used in ref 1 to calculate the vibrational dependence of the alphas, would be a valuable contribution to the subject. A step in this direction appears to have been made in the treatment of planar molecules.[31]

4.Discussion

4.1. Anharmonicity. We now look for the origin of the variations in anharmonicity correction for the two kinds of CH stretching vibration. For simplicity, we focus on ν_1 and ν_{13} in the d_2 species. Table 13 shows a breakdown of the 24.5 cm^{-1} difference obtained using the mtz+ model, while ignoring contributions of less than 0.4 cm^{-1}. (The dtz+, dcct, and mcct results are similar.) Two terms, those involving $x_{r,r}$ and $x_{r,3}$, contribute nearly 70% of the total difference $\Delta_{13} - \Delta_1$. Table 14 in turn shows the major contributions to $x_{1,1}$, $x_{13,13}$, $x_{1,3}$, and $x_{3,13}$ from the different quartic and cubic force constants involved. For both $x_{1,1}$ and $x_{13,13}$, only two terms are of any significance, the single quartic and one cubic term. Both are a little larger for $x_{13,13}$ than those for $x_{1,1}$, but this difference is magnified by a factor of two in $\Delta_{13} - \Delta_1$. The much bigger difference between $x_{3,13}$ and $x_{1,3}$ (including a sign difference) is mostly due to the large contribution of 17.99 cm^{-1} to $x_{1,3}$ arising from the term in $\phi_{1,3,3}{}^2$, although the quartic term also is significant in this respect. The term in $\phi_{1,3,3}{}^2$ is of course that which would be involved if FR were considered to exist between ν_1 and $2\nu_3$. Removal of this term from the second-order treatment would lower ν_1 by 17.99/2 = 9.0 cm^{-1}. A first-order calculation using the harmonic values of ω_1 (3192.7 cm^{-1}) and $2\omega_3$ (3053.7 cm^{-1}), together with the mtz+ value of −143.08 cm^{-1} for $\phi_{1,3,3}$, lowers ν_1 by 8.7 cm^{-1}, suggesting that we are still in the realm where second-order theory is applicable. [A rough calculation applying the same first-order treatment to the G03 anharmonic values of ν_1 (3074.1 cm^{-1}) and $2\nu_3$ (2953.8 cm^{-1}), lowered and raised, respectively, by about 9 cm^{-1}, to simulate the removal of the second-order $\phi_{1,3,3}{}^2$ term, yields a slightly larger Fermi resonance shift of about 13 cm^{-1}.] There is, of course, no simple way of deciding where "normal" anharmonicity, describable by second-order perturbation theory, ends and FR takes over, as the well-known diagram, Figure 70, in Herzberg's classic monograph illustrates.[32] The lack of evidence in the observed vibrational spectra of DFCP for overtone levels associated with modes involving a high proportion of δ_sCH$_2$ motion does suggest that conventionally, at least, Fermi resonance is negligible. However, the present analysis makes it clear that the same cubic force constant, which in other circumstances certainly could produce a substantial degree of FR, is still in DFCP, making a significant contribution to the overall anharmonicity of the symmetric CH stretching vibration.

The identification of differing effects of anharmonicity in symmetric and antisymmetric CH stretching frequencies in DFCP prompts an inquiry as to whether this effect is general for all types of C−H bond. Table 15 lists experimental data for methyl chloride, bromide, and iodide, which show larger Δ values for the antisymmetric mode ω_4 than those for the symmetric modes ω_1, only a part of which arises from the FR involving ν_1, which appears to have been accurately assessed.[6] Table 16 shows some theoretical values of anharmonicity corrections Δ for the CH stretches in ethylene. These include our own calculations with models identical to those used for DFCP and also some published values based on CCSD(T) calculations.[7] The Δ values for the symmetric stretching mode, $\omega_1(a_1)$, and the antisymmetric stretching modes $\omega_5(b_{1g})$ and $\omega_9(b_{2u})$, are all similar. That for the symmetric stretch, $\omega_{11}(b_{3u})$, is markedly different, but here, a Fermi resonance affecting the value of ν_{11} has long been recognized.[33] A current study of dichloromethane indicates that its behavior in the CH stretching region resembles closely that of DFCP.[34] These few examples offer slight evidence to support the suggestion that anharmoncity differences between the two kinds of CH stretching may be linked to the presence of sp^3-type bonding systems and may be absent where the bonding is sp^2. This observation conflicts with the attribution of sp^2-hybridized bonding in cyclopropane in the Walsh model.[35]

TABLE 14: Major Contributions of Cubic and Quartic Potential Constant Terms to Selected x_{ij} from the mtz+ Model (units: cm^{-1})

$x_{1,1}$		$x_{13,13}$		$x_{1,3}$		$x_{3,13}$	
term in:	contrib.	term in:	contrib.	term in:	contrib.	term in:	contrib.
$\phi_{1,1,1,1}^2$	30.34	$\phi_{13,13,13,13}^2$	34.10	$\phi_{1,1,3,3}^2$	−28.15	$\phi_{3,3,13,13}^2$	−34.10
$\phi_{1,1,1}^2$	−57.16	$\phi_{1,13,13}^2$	−64.51	$\phi_{1,1,1}\cdot\phi_{1,3,3}$	14.83	$\phi_{1,3,3}\cdot\phi_{1,13,13}$	15.62
				$\phi_{1,3,3}^{2a}$	17.99[a]	$\phi_{3,13,16}^2$	2.51
				$\phi_{1,3,4}^2$	6.20	$\phi_{3,13,17}^2$	4.79
						$\phi_{3,13,19}^2$	2.34
$\Sigma 2$	−26.82	$\Sigma 2$	−30.41	$\Sigma 4$	10.87	$\Sigma 5$	−8.94
$\Sigma 21$	−27.14[b]	$\Sigma 21$	−31.46[b]	$\Sigma 21$	9.46[b]	$\Sigma 21$	−7.82[b]

[a] This term is greatly reduced if Fermi resonance is invoked between ν_1 and $2\nu_{33}$. [b] Value of x_{ij}.

TABLE 15: Anharmonicity Corrections to CH Stretching Frequencies (cm^{-1}) in CH_3Cl, CH_3Br, and CH_3I

	CH_3Cl[a]			CH_3Br[b]			CH_3I[c]		
	mode 1	mode 4	$\delta\Delta_{4-1}$	mode 1	mode 4	$\delta\Delta_{4-1}$	mode 1	mode 4	$\delta\Delta_{4-1}$
ω_{obsd}	3088.40	3183.33		3095.15	3201.85		3096.12	3212.50	
ν_{obsd}	2967.78	3039.29		2973.18	3056.35		2971.29	3060.08	
ν^{o}_{obsd}[d]	2954.26			2961.32			2962.26		
$\Delta = \omega - \nu$	120.62	144.04	23.4	121.97	145.50	23.5	124.83	152.42	27.6
$\Delta = \omega - \nu^{o}$	134.14	144.04	9.9	135.83	145.50	11.7	133.86	152.42	18.6

[a] Ref 6a. [b] Ref 6b. [c] Ref 6c. [d] Corrected for Fermi resonance with $2\nu_5$ below.

TABLE 16: Comparison of QC-Calculated Anharmonic Corrections $\Delta_i = \omega_i - \nu_i$ (cm^{-1}) to CH Stretching Vibrations in C_2H_4

	ν_{obsd}[a]	Δ_{dtz+}[b]	Δ_{dcct}[b]	Δ_{mtz+}[b]	Δ_{mcct}[b]	Δ_{CCSD}[c]
ν_1 A_g	3022.0	131.4	128.7	138.0	135.8	141.2
ν_5 B_{1g}	3083.4	136.7	134.7	134.8	136.5	143.0
ν_9 B_{2u}	3104.9	139.7	138.2	138.4	139.1	146.2
ν_{11} B_{3u}	2988.6	189.1[d]	169.6[d]	10.3[d]	−74.3[d]	160.1[e]

[a] Observed frequencies from ref 7. [b] This work. [c] From a CCSD(T)/cc-pVTZ calculation, ref 8. Mode numbers as in this reference. [d] Fermi resonance present but not treated. [e] Fermi resonance treated specifically.

It is beyond the scope of the present study to consider whether anharmonicity differences are involved in the stretchings of other types of bonds. Here, we can only explain why our present study throws no light on such differences for the CF bonds present in DFCP. All of our information from G03 is confined to the anharmonic force constants and quantities derived from them associated with normal modes only. Inspection of the PEDs in Tables 8–10 shows that CF stretching contributes significantly to at least four normal coordinates in the A_1 or A′ species vibrations and at least two in the B_1 or A′ modes. Only an anharmonic analysis in terms of individual *valence* coordinates could throw light on anharmonicity differences associated with differing types of CF stretching.

5.Summary

Quantum chemical force fields have been computed for 1,1-difluorocyclopropane (DFCP) with Gaussian 03 (G03) and two B3LYP and two MP2 models at the triple-zeta level. DFCP and its d_2 and d_4 isotopomers are exceptional in having negligible Fermi resonance in the CH and CD stretching regions. Scaling of the force fields has been done in symmetry coordinate space to fit the observed anharmonic frequencies (ν_{obsd}) and "observed" harmonic frequencies (ω_{obsd}) for the three isotopomers. The ω_{obsd} were derived from the ν_{obsd} and anharmonicity constants computed with G03. The need for separate scale factors for different symmetry coordinates was identified, especially for the CH stretching coordinates. The consequences of significant differences between B3LYP and MP2 calculations of CHstretch/CHstretch interaction constants have been explored. The force field obtained with scaling to ν_{obsd} frequencies was used to compute vibration−rotation interaction alphas needed for the semi-experimental structure of DFCP. The several force fields were evaluated by comparing differences between observed and calculated frequencies and observed and calculated centrifugal distortion constants (CDCs). The prediction of CDCs with G03 is good enough to aid the fitting of limited sets of rotational transitions. Anharmonicity corrections for the CH_2 stretching frequencies, which differ significantly for symmetric and antisymmetric modes, have been traced out in the dependence on cubic and quartic force constants computed with G03. Deficiencies in G03 code for computing vibrational and rotational constants necessitate special care in the applications reported here.

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Supporting Information Available: Frequency fits for the B3LYP and MP2 force fields scaled both to ν_{obsd} and to ω_{obsd} (Table S1, d_0, Table S2, d_4, Table S3, d_2); MP2/6-311G** force constants scaled to ν_{obsd} (Table S4); predictions of ν_{obsd} for the d_1 and d_3 isotopomers from the scaled MP2/6-311G** force field (Table S5); predictions of α's for the five isotopomers used for the semi-experimental r_e structure (Table S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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