Ab Initio Vibrational Analysis of Cyclopropene, Its Fluoro Derivatives, and Their Deutero Analogues

M. S. Baird,[†] K. Spencer,[†] S. V. Krasnoshchiokov,[‡] Yu. N. Panchenko,*,[§] N. F. Stepanov,[‡] and G. R. De Maré[∥]

University of Wales, Department of Chemistry, Bangor, Gwynedd LL57 2UW, United Kingdom, Laboratory of Molecular Structure and Quantum Mechanics, Chair of Physical Chemistry, Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119899, Russian Federation, Laboratory of Molecular Spectroscopy, Chair of Physical Chemistry, Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119899, Russian Federation, and Laboratoire de Chimie Physique Moléculaire, Faculté des Sciences, CP 160/09, Université Libre de Bruxelles, av. F.-D. Roosevelt 50, B-1050 Brussels, Belgium

Total geometry optimization and computation of the ab initio force fields for cyclopropene and six of its fluoro derivatives are carried out at the HF/6-311G* level. The HF/6-311G*//HF/6-311G* force field of cyclopropene is scaled using the empirical scale factors determined only from the experimental vibrational frequencies of the light isotopic species of cyclopropene. The scaled force field obtained is used to calculate the vibrational frequencies for seven deutero analogues of cyclopropene and six of its fluoro derivatives. The scale factors for the >CF$_2$ moiety of 3,3-difluorocyclopropene are refined using the experimental vibrational frequencies of its light isotopic species. The refined set of scale factors is transferred to the HF/6-311G*// HF/6-311G* force field of 1,2,3,3-tetrafluorocyclopropene. The experimental vibrational frequencies of this molecule are used to refine the scale factors for the =C−F moieties. The scale factors obtained, together with the scale factors for cyclopropene, are used to predict the vibrational frequencies of the 3-fluoro-, 1,3,3-trifluoro-, 1-fluoro-, and 1,2-difluorocyclopropenes. The vibrational problems for all the molecules just mentioned and for some of their deutero analogues are solved using the HF/6-311G*//HF/6-311G* force fields corrected by the corresponding refined sets of scale factors. The complete assignments of all the fundamental frequencies are given. Some peculiarities of the vibrational spectra of this molecular series are discussed.

Introduction

Cyclopropene (**I**) has been subjected repeatedly to the determination of its structure (Figure 1) and to vibrational analysis.[1−13] The most recent vibrational analysis of **I**[13] was performed using the HF/6-31G*//HF/6-31G* force field and Pulay's scaling procedure.[14−17]

Two other recent vibrational analyses of **I** were based on an ab initio calculation[10] and an empirical potential function (determined by solution of the inverse vibrational problem[12]). The former involved scaling the quantum mechanical force field.[10] Each of the diagonal force constants was given a separate scale factor, and a single scale factor was used for all the off-diagonal force constants. The scale factors were determined using the experimental frequencies of four (light and deuterated) isotopomers of **I**, possessing C_{2v} symmetry. However, it has been shown[18,19] that this procedure has certain disadvantages: it is based on the assumption that the relative accuracy of the diagonal and the off-diagonal force constants determined by the ab initio methods at a given level of theory is different and that all the off-diagonal force constants can be corrected by the same scale factor. In the second case, an
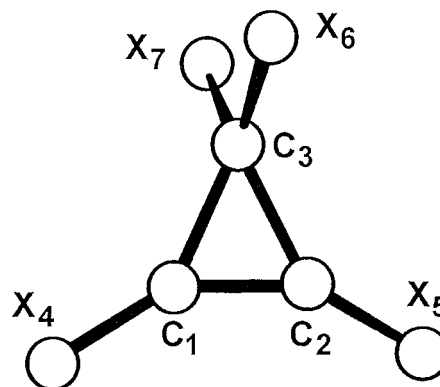

Figure 1. Structure of cyclopropene (**I**) and its fluorinated derivatives. The numbering of atoms is used throughout the text. X = H or F.

empirical potential function was fitted to the vibrational fundamentals of eight of the nine possible hydrogen−deuterium isotopomers of **I**.[12] Comparison of the results obtained in these two vibrational analyses reveals contradictions in the assignments of some fundamentals, which will be discussed later.

In contrast to the attention given to **I**, few studies have been conducted on fluoro-substituted cyclopropenes.[20−26] The vibrational spectra of the light and deuterated isotopomers of 3,3-difluorocyclopropene (**II**),[23] 3-fluorocyclopropene (**III**),[25] and 1,3,3-trifluorocyclopropene (**IV**)[21] have been reported. For these molecules and perfluorocyclopropene (**V**),[24] the inverse vibra-

* To whom correspondence should be addressed. E-mail: panchenk@ physch.chem.msu.su.
† University of Wales.
‡ Laboratory of Molecular Structure and Quantum Mechanics.
§ Laboratory of Molecular Spectroscopy.
∥ Laboratoire de Chimie Physique Moléculaire.

TABLE 1: Experimental and Calculated (HF/6-311G*) Geometrical Parameters (Angstroms and Degrees) of Cyclopropene (I), 3,3-Difluorocyclopropene (II), 3-Fluorocyclopropene (III), 1,2,3,3-Tetrafluorocyclopropene (V), 1,3,3-Trifluorocyclopropene (IV), 1,2-Difluorocyclopropene (VI), and 1-Fluorocyclopropene (VII)

	I C_{2v}		II C_{2v}		III C_s	IV C_s	V C_{2v}		VI C_{2v}	VII C_s
parameter	MW ref 4	calc	MW ref 22	calc	calc	calc	exptl[a]	calc	calc	calc
r(C=C)	1.296	1.275	1.321	1.299	1.288	1.287	1.307	1.282	1.259	1.265
r(C−C)	1.509	1.498	1.438	1.435	1.458	1.463(H)	1.461	1.446	1.496	1.542(H)
r(C−C)						1.422(F)				1.460(F)
r(=C−H)	1.072	1.068	1.075	1.069	1.068	1.068				1.065
r(=C−F)						1.286	1.315	1.284	1.292	1.293
r(>C−H)	1.088	1.083			1.076				1.084	1.083
r(>C−F)			1.365	1.338	1.369	1.334	1.361	1.334		
∠C=C−H	149.89	149.91	148.38	148.54	149.45	151.52				153.71
∠C=C−F						147.40	149.9	149.95	151.73	148.52
∠H−C−H	114.66	113.20							113.03	113.27
∠F−C−F			105.48	105.79		105.90	105.4	105.85		
∠H−C−F					108.00					
∠C−C(H₂)−C		50.38							49.75	49.76
∠C−C(F₂)−C			54.60	53.83		52.98	53.2	52.63		
∠C−C(HF)−C					52.42					
∠C−C=C−H					177.17					
∠C−C−C−H					177.38					
∠C=C−C−H					109.88					
∠C=C−C−F					105.83					
∠H−C−C−H					72.74					
∠H−C−C−F					71.55					
∠H−C=C−H					0.00					

[a] ED/MW/LC (liquid crystal ¹⁹F NMR spectrum) r_g, ∠$_α$ (see ref 26).

TABLE 2: Experimental and Calculated Vibrational Frequencies of Cyclopropene and Its Deuterated Isotopomers (cm⁻¹)[a]

			d_0		$1,2$-d_2		$3,3$-d_2		d_4	
ν	assignment	C_{2v} species	exptl ref 12	calc	exptl ref 12	calc	exptl ref 12	calc	exptl ref 12	calc
1	ν(C−H)s.str	a_1	3158	3163	2435	2420	3151	3163	2435	2421
2	ν(CH₂)s.str		2909	2925	2904	2926	2144	2118	2142	2117
3	ν(C=C)str		1653	1652	1572	1561	1648	1640	1548	1532
4	δ(CH₂)sciss		1483	1488	1460	1469	1154	1148	1147	1145
5	ν(C−C)s.str		1110	1108	1094	1086	1048	1044	1023	1011
6	ρ(C−H)s.rock		905	893	669	654	890	876	639	650
7	τ(CH₂)twist	a_2	(996)	995	986	994	736	730	749	766
8	χ(C−H)s.wag		820	817	(665)	659	815	826	(637)	628
9	ν(C−H)as.str	b_1	3124	3119	2320	2293	3118	3119	2313	2293
10	χ(CH₂)wag		1043	1043	1042	1042	(858)	885	885	907
11	ρ(C−H)as.rock		1011	1022	880	892	1014	1022	839	839
12	ν(C−C)as.str		769	772	680	675	710	699	637	627
13	ν(CH₂)as.str	b_2	2995	2979	2995	2979	2260?	2219	2262?	2219
14	ρ(CH₂)rock		1088	1084	1080	1083	853	849	839	846
15	χ(C−H)as.wag		569	574	431	434	562	565	424	427

			1-d_1		$1,3,3$-d_3			3-d_1			$1,3,$-d_2	
ν	assignment	C_s	exptl ref 12	calc	exptl ref 12	calc	C_s	exptl ref 12	calc	C_1	exptl ref 12	calc
1	ν(C−H)s.str	a'	3133	3142	3133	3142	a'	3149	3163	a	3134	3142
2	ν(CH₂)s.str		2905	2925	2144	2117		2963	2953		2972	2953
3	ν(C=C)str		1607	1600	1593	1583		1649	1644		1598	1587
4	δ(CH₂)sciss		1480	1481	1148	1146		1354	1357		1348	1355
5	ν(C−C)s.str		1106	1099	1044	1038		1102	1103		1104	1095
6	ρ(C−H)s.rock		678	670	647	636		880	869		771	774
7	τ(CH₂)twist	a''	(991)	994	725	709	a''		841		(821)	837
8	χ(C−H)s.wag		760	759	770	787		817	809		749	736
9	ν(C−H)as.str	a'	2376	2359	2379	2360		3117	3119		2384	2359
10	χ(CH₂)wag		1041	1042	862	879		1021	1024		1020	1023
11	ρ(C−H)as.rock		974	981	966	968		1009	1022		979	983
12	ν(C−C)as.str		801	801	(770)	758		718	709		657	648
13	ν(CH₂)as.str	a''	2994	2979	2261?	2219	a'	2203?	2167		2184	2167
14	ρ(CH₂)rock		1087	1083	850	848		927	921		903	898
15	χ(C−H)as.wag		479	483	471	473		565	569		475	478

[a] Frequencies in parentheses are based on indirect experimental evidence, including product rule calculations or combination tones (see ref 12).

tional problems were solved and complete vibrational assignments given. However, to the best of our knowledge, the only published report of ab initio vibrational analysis of any fluoro

derivative of **I** at a current level of theory (for example, HF/6-311G* [27]) is the vibrational analysis of **V** at the MP2/DZP//MP2/DZP level given in ref 26. Therefore, it is of interest to

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TABLE 3: Scale Factors for the HF/6-311G*//HF/6-311G* Force Fields of Cyclopropene (I), 3,3-Difluorocyclopropene (II), 1,2,3,3-Tetrafluorocyclopropene (V), 3-Fluorocyclopropene (III), 1,3,3-Trifluorocyclopropene (IV), 1,2-Difluorocyclopropene (VI), and 1-Fluorocyclopropene (VII)

coordinate	C_3H_4 I A	$C_3H_2F_2$ II B	C_3F_4 V C	C_3HF_3 IV A/C	C_3H_3F III A/B	VI–VII A/C
C=C str	0.786	0.786	0.786	0.786	0.786	0.786
=C–H rock	0.786	0.786		0.786	0.786	0.786
=C–F rock			0.778	0.778		0.778
C–C str	0.792	0.792	0.792	0.792	0.792	0.792
=C–H str	0.831	0.831		0.831	0.831	0.831
=C–F str			0.763	0.763		0.763
C–H str	0.840				0.840	0.840
C–F str		0.782	0.782	0.782	0.782	
CH₂ def	0.813				0.813	0.813
CF₂ def		0.836	0.836	0.836		
CH₂ wag	0.782				0.782	0.782
CF₂ wag		0.824	0.824	0.824		
=C–H wag	0.707	0.707		0.707	0.707	0.707
=C–F wag			0.655	0.655		0.655

perform a joint ab initio vibrational analysis of the related molecules (including 1,2-difluorocyclopropene (**VI**) and 1-fluorocyclopropene (**VII**) for which the vibrational spectra have not been measured yet) and to obtain information about effects of the fluoro substitution on the vibrational frequencies of the cyclopropene ring.

Method and Results

The geometries of **I** and all the fluoro derivatives under investigation (**II–VII**) were completely optimized with *GAUSS-IAN 94*[28] using the Hartree–Fock approximation and the split-valence 6-311G* basis set (HF/6-311G*).[27] The geometrical parameters are listed in Table 1 with the corresponding experimental data for **I**, **II**, and **V**. The Cartesian force constants were calculated at the HF/6-311G*//HF/6-311G* level. These constants were transformed into local (valence) symmetry coordinates[29] and scaled according to Pulay's method.[14–17] Only the experimental frequencies of **I**-d_0 (Table 2) were involved in the scaling procedure. The optimized ab initio geometries were used without any empirical correction. The theoretical justification of this technique[14,15] was given in refs 16 and 17. The scale factors obtained for the HF/6-311G*//HF/6-311G* force field of **I** are given in Table 3, column A. The vibrational frequencies of **I** and of seven deuterated isotopomers, calculated using the scaled force field of **I,** are listed in Table 2.

For the fluoro derivatives, at the first step the scale factors obtained for **I** were transferred to the quantum mechanical force fields of **II**, **V**, **IV**, and **III** and their vibrational frequencies were calculated (columns A in Tables 4, 5, 6, and 7, respectively). Then, only the scale factors for the force constants concerning the coordinates of the >CF₂ moiety of **II** were optimized using the corresponding experimental frequencies of its light isotopomer.[23] The partially refined set of scale factors (Table 3, column B) was applied to the solution of the vibrational problem for **II** and its deuterated isotopomers (Table 4, columns B).

At the second step, the set of scale factors in Table 3, column B was utilized without modification for correction of the HF/6-311G*//HF/6-311G* force field of **V**, and its theoretical frequencies were calculated. (Table 5, column B). The calculated and experimental frequencies of this molecule are collected in Table 5. Then, only the scale factors for the vibrations of the =C–F moieties were optimized using the experimental frequencies of **V** to yield the set given in Table 3, column C. Combinations of these sets of scale factors were used for correction of the force fields of **III**, **IV**, **VI**, and **VII**. The experimental and calculated frequencies of these molecules are given in Tables 6–8.

The juxtaposition of the experimental vibrational frequencies of **I–V** is given in Table 9.

To demonstrate inverse isotopic shifts in the vibrational frequencies of **II** and its deutero analogues, the vibrational problems were solved for molecules with the masses of the H atoms varied simultaneously from 1 up to 2 (vide infra). The results are shown in Figure 2. The vibrational problems were also solved for molecules with masses varied simultaneously from 1 up to 19 for the H atoms at C_1 and C_2 in **II** and with masses from 19 down to 1 for the F atom at C_1 in **IV**. Some of the results of these calculations are presented in Figures 3 and 4. All the normal modes are characterized by the dominant terms in the potential energy distribution (PED). The numbering of the atoms is shown in Figure 1. The definition of the coordinates and the scaled force constants are given as Supporting Information in Tables 10-17.

Bond orders were calculated at the HF/6-311G*//HF/6-311G* level with *MONSTERGAUSS*[30] using Mayer's method.[31]

Discussion

Geometrical Parameters. The agreement between the calculated and experimental geometrical parameters of **I**, **II**, and **V** may be accepted as satisfactory (see Table 1). The influence

TABLE 4: Experimental and Calculated Vibrational Frequencies of 3,3-Difluorocyclopropene (II) and Its Deuterated Isotopomers (cm⁻¹)

ν	assignment	C_{2v}	$C_3H_2F_2$ exptl ref 23	calc A	calc B	$C_3D_2F_2$ exptl ref 23	calc B	C_s	C_3HDF_2 exptl ref 23	calc B
1	ν(=C–H)str	a_1	3150	3156	3156	2429	2406	a'	3148	3138
2	ν(C=C)str		1598	1600	1598	1509	1498		1557	1546
3	ν(C–C)s.str		1343	1358	1347	1339	1338		1341	1342
4	χ(=C–H)s.rock		946	942	936	657	650		718	712
5	ν(CF₂)s.str		769	775	761	820	804		823	812
6	δ(CF₂)sci		500	498	504	487	490		505	508
7	χ(=C–H)s.wag	a_2	883	862	862	732	720	a''	827	809
8	τ(CF₂)twist		393	386	391	352	345		351	348
9	ν(=C–H)as.str	b_1	3128	3119	3119	2322	2300	a'	2371	2354
10	ν(C–C)as.str		1131	1125	1127	1081	1075		1120	1103
11	ρ(=C–H)as.rock		968	963	968	833	832		953	954
12	χ(CF₂)wag		522	512	523	470	466		478	479
13	ν(CF₂)as.str	b_2	1094	1133	1098	1093	1096	a''	1095	1097
14	χ(=C–H)as.wag		680	665	664	587	579		613	603
15	ρ(CF₂)rock		416	414	418	356	354		403	406

TABLE 5: Experimental and Calculated Vibrational Frequencies of 1,2,3,3-Tetrafluorocyclopropene (V) (cm^{-1})

| | | | C$_3$F$_4$ | | | |
| | | | | calculation | | |
ν	assignment	C_{2v} species	exptl ref 24	A	B	C
1	ν(=C−F)s.str	a_1	929	941	929	915
2	ν(C=C)str		1940	1973	1972	1947
3	ν(C−C)s.str		1367	1387	1375	1375
4	ρ(=C−F)s.rock		243	244	244	243
5	ν(CF$_2$)s.str		709	719	711	702
6	δ(CF$_2$)sciss		509	504	510	508
7	χ(=C−F)s.wag	a_2	616	634	636	619
8	τ(CF$_2$)twist		205^a	203	205	203
9	ν(=C−F)as.str	b_1	892	896	899	886
10	ν(C−C)as.str		1331	1372	1373	1335
11	ρ(=C−F)as.rock		251	257	259	258
12	χ(CF$_2$)wag		781	771	782	780
13	ν(CF$_2$)as.str	b_2	1109	1145	1109	1109
14	χ(=C−F)as.wag			185	186	180
15	ρ(CF$_2$)rock		551	544	548	544

^{a} Corrected value from liquid-phase Raman spectrum (see ref 26).

TABLE 6: Experimental and Calculated Vibrational Frequencies of 1,3,3-Trifluorocyclopropene (IV) (cm^{-1})

| | | | C$_3$HF$_3$ | | C$_3$DF$_3$ | |
| | | | | calc | | calc |
ν	assignment	symmetry species	exptl ref 21	A	A/C	exptl ref 21	A/C
1	ν(=C−H)str	a'	3157	3153	3153	2408	2379
2	ν(C=C)str		1793	1808	1790	1746	1739
3	ν(C−C)s.str		1404	1406	1395	1398	1388
4	ρ(=C−F)rock		281	279	280	280	279
5	ν(CF$_2$)s.str		764	778	760	764	755
6	δ(CF$_2$)sciss		500	499	506	473	476
7	χ(=C−H)wag	a''	788	782	778	680	676
8	τ(CF$_2$)twist		380	390	394	333	341
9	ν(=C−F)str	a'	854	855	854	893	884
10	ν(C−C)as.str		1160	1191	1175	1140	1153
11	ρ(=C−H)rock		993	1001	995	810	814
12	χ(CF$_2$)wag		613	609	612	539^a	556
13	ν(CF$_2$)as.str	a''	1103	1142	1106	1102	1106
14	χ(=C−F)wag		204	196	194	205	194
15	ρ(CF$_2$)rock		570	567	564	559	554

^{a} Calculated from isotope product rule.

of electron correlation is demonstrated by the results of geometry optimization for **I** at the MP2(FC)/6-31G level[32] and for **V** at the HF/DZP, HF/TZ2P, MP2/DZP, and MP2/TZ2P levels.[26] It was shown in ref 26 that, as is expected,[33] an account of electron correlation is essential for quantitative agreement between theory and experiment. However, it should be kept in mind that we deal with different structure definitions; they are, the theoretical equilibrium geometry (r_e) and the experimental r_a or r_g geometrical parameters.

Except for **III**, all the molecules have five atoms in the symmetry plane defined by the three-membered ring. In **III**, the asymmetry of the >CHF group causes the =CH hydrogen atoms to move out of the ring plane (i.e., toward the F atom). However, the most interesting feature of the results given in Table 1 is the variation of the optimized structural parameters of the three-membered ring. It is predicted that the substitution of only one H atom by an F atom at C3 (i.e., in **III**) would cause the formal single C−C bond lengths (r(C−C)) to decrease by 0.040 Å and the formal C=C double bond (r(C=C)) to increase by 0.013 Å. These remarkable changes are followed by a decrease in r(C−C) by 0.025 Å and an increase in r(C=C) by 0.013 Å on substitution of the second H atom at C3 by fluorine (in **II**). The overall changes on fluorine substitution at C3 are predicted to be −0.065 Å and +0.024 Å for r(C−C)

TABLE 7: Experimental and Calculated Vibrational Frequencies of 3-Fluorocyclopropene (III) (cm^{-1})

| | | | C$_3$H$_3$F | | | C$_3$D$_3$F | |
| | | | | calc | | | |
ν	assignment	C_s species	exptl ref 25	A	A/B	exptl ref 25	calc A/B
1	ν(=C−H)str	a'	3162	3160	3160	2446	2414
2	ν(CHF)s.str		3032	3039	3039	2265	2239
3	ν(C=C)str		1623	1616	1616	1522	1507
4	δ(CHF)sciss		1329	1349	1349	966	971
5	ν(C−C)s.str		1200	1205	1199	1186	1192
6	ρ(=C−H)s.rock		914^a	906	906	663	675
7	τ(CHF)twist	a''	876	876	876	658	645
8	χ(=C−H)s.wag		860	839	840	730	730
9	ν(=C−H)as.str	a''	3122	3119	3119	2326	2297
10	χ(CHF)wag		446	433	433	387	385
11	ρ(=C−H)as.rock		1037	1041	1041	852	845
12	ν(C−C)as.str		1060	1072	1072	995	997
13	ν(CHF)as.str	a'	956	975	949	938	928
14	ρ(CHF)rock		457	452	452	383	379
15	χ(C−H)as.wag		660	645	643	558	548

^{a} Original attribution of this vibration is the Raman band at 936 cm^{-1} in liquid phase (see ref 25). The 914 cm^{-1} band is measured in IR spectrum in crystalline phase.

TABLE 8: Calculated Vibrational Frequencies of 1,2-Difluorocyclopropene (VI) and 1-Fluorocyclopropene (VII) (cm^{-1})

ν	assignment	species	C$_3$H$_2$F$_2$ (VI)	species	C$_2$H$_3$F (VII)
1	ν(=C−F)str	a_1	748	a'	3171
2	ν(C=C)str		2000		1828
3	ν(C−C)s.str		1185		1236
4	ρ(=C−F)s.rock		279		922
5	ν(CH$_2$)s.str		2919		2927
6	δ(CH$_2$)sci		1510		1499
7	χ(=C−F)s.wag	a_2	516	a''	706
8	τ(CH$_2$)twist		986		987
9	ν(=C−F)as.str	b_1	799	a'	668
10	ν(C−C)as.str		1245		995
11	ρ(=C−F)as.rock		436		420
12	χ(CH$_2$) wag		1080		1052
13	ν(CH$_2$)as.str	b_2	2973	a''	2983
14	χ(=C−F)as.wag		228		339
15	ρ(CH$_2$)rock		1100		1087

TABLE 9: Juxtaposition of the Experimental Vibrational Frequencies of Cyclopropene (I), 3-Fluorocyclopropene (III), 3,3-Difluorocyclopropene (II), 1,3,3-Trifluorocyclopropene (IV), and 1,2,3,3-Tetrafluorocyclopropene (V) (cm^{-1})^a

| | | C$_3$H$_4$ **I** | C$_3$H$_3$F **III** | C$_3$H$_2$F$_2$ **II** | C$_3$HF$_3$ **IV** | C$_3$F$_4$ **V** |
ν	assignment	ref 12	ref 25	ref 23	ref 21	ref 24
1	ν(=C−H(F))str	3158	3162	3150	3157	929
2	ν(C=C)str	1653	1623	1598	1793	1940
3	ν(C−C)s.str	1110	1200	1343	1404	1367
4	ρ(=C−H(F))s.rock	905	914	946	281	243
5	ν(CH$_2$(F$_2$))s.str	2909	3032	769	764	709
6	δ(CH$_2$(F$_2$))sci	1483	1329	500	500	509
7	χ(=C−H(F))s.wag	820	860	883	788	616
8	τ(CH$_2$(F$_2$))twist	(996)	876	393	380	214
9	ν(=C−H(F))as.str	3124	3122	3128	854	892
10	ν(C−C)as.str	769	1060	1131	1160	1331
11	ρ(=C−H(F))as.rock	1011	1037	968	993	251
12	χ(CH$_2$(F$_2$))wag	1043	446	522	613	781
13	ν(CH$_2$(F$_2$))as.str	2995	956	1094	1103	1109
14	χ(=C−H(F))as.wag	569	660	680	204	(180)
15	ρ(CH$_2$(F$_2$))rock	1088	457	416	507	551

^{a} Values in parentheses are the calculated frequencies.

and r(C=C), respectively. This concept is in good agreement with the experimental data: −0.061 Å and +0.024 Å for r(C−C) and r(C=C) on going from **I** to **II**, respectively. In the
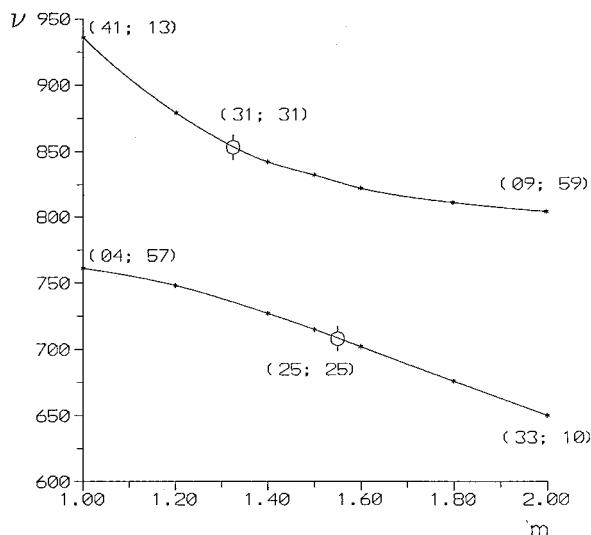
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Figure 2. Dependence of the theoretical frequencies 936 cm^{-1} (ν_4, ρ(=C—H)s.rock) and 761 cm^{-1} (ν_5, ν(CF$_2$)s.str) of 3,3-difluorocyclopropene (**II**); (see Table 4, column B) on the hypothetical (equal) masses of the H atoms. The contributions (percentage) of the =C—H symmetric rock and CF$_2$ symmetric stretch coordinates into the PEDs for the given masses are given in brackets. Points in circles correspond to the equal contributions of these coordinates into the PED.
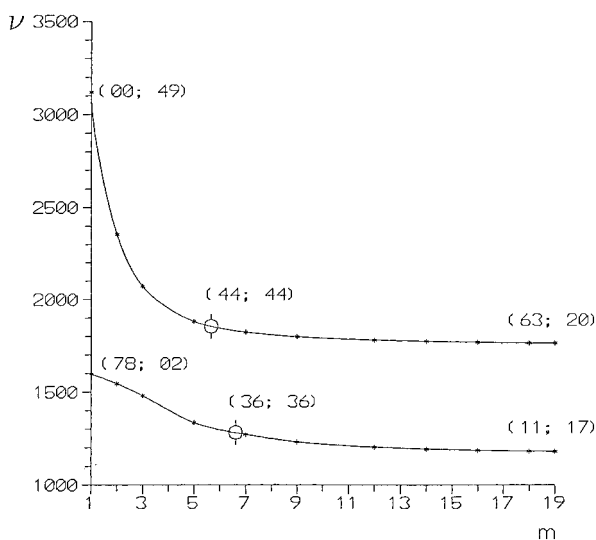
Figure 3. Dependence of the theoretical frequencies 1598 cm^{-1} (ν_2, ν(C=C)str) and 3119 cm^{-1} (ν_9, ν(=C—H)str) of 3,3-difluorocyclopropene (**II**; see Table 4, column B) on the hypothetical masses of the H atoms varied simultaneously from 1 up to 19. The contributions (percentage) of the C=C and =C—H stretch coordinates into the PEDs for the given masses are presented in brackets. Points in circles correspond to the equal contributions of these coordinates into the PED.

asymmetric molecule **IV**, r(C—CH) and r(C—CF) are shorter than r(C—C) in **I** by 0.035 and 0.076 Å, respectively (Table 1, calculated values), indicating an important additional effect of substitution by fluorine at C1. In general, the present results (Table 1) are in agreement with the simple scalar superposition rule.[34]

Vibrational Analysis

Cyclopropene (I). The vibrational analyses of **I** in refs 7, 10, and 12 resulted in reliable frequency assignments for the d_0-isotopomer (see Table 2). This assignment of the experimental vibrational spectrum of **I** is also supported by our calculations with the HF/6-311G*//HF/6-311G* quantum me-
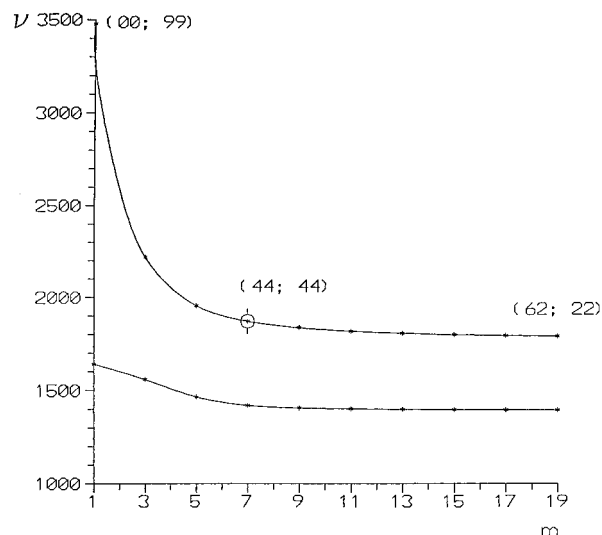
Figure 4. Dependence of the theoretical frequencies 1790 cm^{-1} (ν_2, ν(C=C)str) and 1395 cm^{-1} (ν_3, ν(C—C)s.str) of 1,3,3-trifluorocyclopropene (**IV**; see Table 6, column A/C) on varying the hypothetical mass of the F atom at C$_1$ from 19 down to 1. The contributions (percentage) of the C=C stretch and C—C symmetric stretch coordinates into the PEDs for the given masses are presented in brackets. The ν-(C—C)str frequency is taken instead of ν(=C—F)str because of the great mixing of these vibrations, which is also the reason that the contributions into the PED are not indicated for the lower curve.

chanical force field corrected by a single scale factor, 0.8.[35] In the case of **I**, the assignments are facilitated by the small number of fundamental frequencies in each symmetry species.

It is worthwhile to discuss only the position of the band assigned to ν_3 (ν(C=C)str.). Indeed, two "spikes" with frequencies of 1649.3 and 1663.3 cm^{-1} were observed in the IR spectrum of **I** in ref 3. These spikes were assigned as the P and R branches of ν_3 with the band center at 1656.4 cm^{-1}. Approximately at the same time, two sharp bands at 1653 and 1664 cm^{-1} were also observed in ref 2. The first one (1653 cm^{-1}) was assigned to the Q branch of ν_3 and the second one to a combination or overtone that is intensified by Fermi resonance. The same explanation was also given in ref 12 where appearance of the higher frequency band was attributed to the combination tone $\nu_{14} + \nu_{15} = 1657$ cm^{-1}. Nevertheless, the recent investigation[7] of the vibrational spectrum of **I**-d_0 gives the value of ν_3 as 1653 cm^{-1}. In all the previous calculations of vibrational frequencies, the 1653 cm^{-1} frequency was also used as ν_3.[2,6,10,12,13] The same frequency was utilized for calculation of the scale factors in the present work. However, all the calculated frequencies for deutero derivatives turned out to be lower than the corresponding experimental frequencies (see Table 2). This result obviously means that the appearance of two bands in the 1650 cm^{-1} region is brought about by the presence of two bands whose positions and intensities are disturbed by Fermi resonance; they are ν_3 and $\nu_{14} + \nu_{15}$ as was supposed in refs 2 and 12. However, the deviations of the calculated ν_3 frequencies for the majority of the deutero derivatives are within the usual accuracy for such calculations (see Table 2), which was a main reason in the present calculations to consider the 1653 cm^{-1} frequency as the experimental value for ν_3. Corrections of the experimental frequency ν_3 by 3.4 or 5.5 cm^{-1} (see refs 3 and 2, respectively) could change the coresponding scale factor which is apparently somewhat too small.

Deuterated Isotopomers of I. The majority of the predicted frequencies for the deuterated isotopomers of **I** support the assignments given in refs 7, 10, and 12. (Only those from ref

12, reorganized according to the vibrational assignments, are presented in Table 2.[36])

The present calculations allow us to support our previous choice[13] between the versions of assignments suggested in refs 7 and 10 and in ref 12, respectively. Indeed except for **I**-3,3-d_2 and **I**-d_4, the agreement between our calculated frequencies for ν_{10} ($\chi(CH_2)$wag), ν_{11} ($\rho(C-H)$as.rock), and ν_{14} ($\rho(CH_2)$-rock) and the experimental frequencies with the same assignments[7,10,12] is very good. In refs 7 and 10, the frequency 863 cm^{-1} was assigned to ν_{10} and ν_{14} in **I**-3,3-d_2 and to ν_{11} and ν_{14} in **I**-d_4. In contrast, in ref 12, bands at ~858 cm^{-1} and 853 cm^{-1} were suggested as belonging to ν_{10} and ν_{14} in **I**-3,3-d_2. In the case of **I**-d_4, a band at 839 cm^{-1} was assigned to both ν_{11} and to ν_{14}.[12] The present calculation reveals that the 839 cm^{-1} band should indeed be assigned to both ν_{11} and ν_{14} in **I**-d_4.

The assignment of the frequency, 853 cm^{-1}, to ν_{14} in **I**-3,3-d_2[12] is also supported. However, the calculated frequency for ν_{10} is 885 cm^{-1}. From the aforementioned considerations, the frequencies (863 cm^{-1} and ~858 cm^{-1}) suggested in refs 7, 10, and 12 do not seem to be reasonable experimental counterparts to our calculated value. Some imperfect assignments in ref 10 may have arisen as a consequence of the scaling scheme used and as a result of the large number of scale factors (16) used in that work. Thus, the experimental attribution of ν_{10} ($\chi(CH_2)$wag) in **I**-3,3-d_2 obviously remains to be solved.

The calculated frequencies for the antisymmetric stretching vibrations, ν_{13}, of the $>CH_2$, $>CHD$, and $>CD_2$ moieties seem to be underestimated by ~16, 30, and 40 cm^{-1}, respectively. It was possible to examine the experimental spectra of **I**-1,3-d_2 in ref 12. The region of the IR gas-phase spectrum of this molecule corresponding to the antisymmetric stretches has three medium intensity maxima with the C shapes at 2194, 2203, and 2211 cm^{-1}. The Raman spectrum in this region consists of only two polarized bands at 2184 and 2201 cm^{-1}, with intensities that were evaluated as strong and medium, respectively.[12] This experimental feature makes it possible to assign the Raman band at 2184 cm^{-1} as $\nu(>CHD)$as.str, rather than the IR band at 2194 cm^{-1} (see Table 2). Obviously, the corresponding regions of the spectra of the other partially deuterated isotopomers should also be subjected to an analogous reexamination. However, it is necessary to keep in mind the large anharmonicity inherent in the $>CH_2$, $>CHD$, and $>CD_2$ moieties stretching vibrations that may not be totally accounted for by the scaling procedure.

The vibrational analysis of **I** and of seven deuterated isotopomers, carried out using the refined scaled HF/6-311G*/ /HF/6-311G* force field of **I**, corroborates the assignments of ref 13 completely.

3,3-Difluorocyclopropene (II) and Its Deuterated Isotopomers. Transferring the scale factors determined for **I**-d_0 (Table 3, column A) to the force field of **II** resulted in rather good agreement between the calculated and experimental frequencies of **II**-d_0 (see Table 4, column A). This result is obviously connected with the similarity of the electronic structures of the H and F atoms due to their positions in the Mendeleev Periodic System of chemical elements (i.e., their electronic structures are similar as they each require one electron to fill their outer shell). Indeed, the deviations from the experimental data are rather small for the majority of the calculated frequencies.[23] An exception is the relative frequencies for ν_{10} ($\nu(C-C)$as.str) and ν_{13} ($\nu(CF_2)$as.str) (see Table 4, column A). In ref 23, Table 2, the shapes of the ν_{10} and ν_{13} bands are given as C and B, respectively, which does not seem to correspond to their symmetry species. Therefore, the refinement of scale factors for the $>CF_2$ moiety was performed

for the two alternative assignments of these frequencies: $\nu_{10} = 1131$ cm^{-1} and $\nu_{13} = 1094$ cm^{-1} and vice versa. Upon transferring these sets of scale factors to the quantum mechanical force fields of the other fluoro derivatives of **I**, the best agreement between the calculated and experimental frequencies was found for the set based on the assignments proposed in ref 23. Therefore, the assignments in ref 23 of the 1131 cm^{-1} and 1094 cm^{-1} bands of **II** to ν_{10} and ν_{13}, respectively, are maintained (Table 4, column B). Results obtained with this scaled force field for the light and deuterated species of **II** are also listed in Table 4. In contrast to ref 23, the present choice of vibrational coordinates and scaled force field of **II** led to unambiguous assignments of ν_{13} ($\nu(CF_2)$as.str) for all three isotopomers, according to the PED. Note that in these three isotopic species, strong contributions of the C–C and C–F stretch coordinates into the form and the PED's of the normal modes of ν_3 and ν_5 are observed. In the case of **II**-d_2 the ν_{14} and ν_{15} vibrations are also mixed.

The inverse isotopic shift of ν_5 upon deuteration of **II** is the most interesting result of this analysis (Table 4). (For other examples see refs 37–39 and references therein.) Indeed, increasing the hypothetical mass of the H atoms in the =C–H moieties of **II** from 1 to ~1.4 gives rise to variations of the modes of ν_4 and ν_5. Thus, the contributions of the =C–H rock and C–F stretch coordinates into the form and the PED's of these normal modes become equal at the special points marked on Figure 2. A further increase of mass up to 2 results in a substantial increase of the contribution of the C–F stretch coordinate into the PED of the upper frequency curve and the growth of the =C–H rock contribution into the PED of the lower frequency curve. This effect results in ν_5 increasing by 50 cm^{-1} when going from **II**-d_0 to **II**-d_2 or to **II**-d_1. This increase does not violate the well-known Rayleigh rule.[40]

1,2,3,3-Tetrafluorocyclopropene (V). The A and B scale factor sets in Table 3 were used to correct the HF/6-311G*// HF/6-311G* force field of **V**, and its fundamental frequencies were calculated. It can be seen in Table 5 that it is possible to predict the vibrational spectrum rather accurately and to maintain, in general, the assignments suggested in ref 24.

A particular difficulty is connected with ν_{14}, the antisymmetric wagging of the =C–F bonds ($\chi(=C-F)$as.wag). In ref 24, this mode was attributed to the experimental band at 251 cm^{-1}. However, the present calculations reveal that the frequency of this vibration should be situated in the region around 180 cm^{-1}. The same result was also obtained in ref 26 using the MP2/ DZP//MP2/DZP force field and Pulay's scaling method. However, the authors of ref 26 mentioned that MW vibrational satellite intensities show that the $>CF_2$ (a_2) twisting mode is the lowest frequency mode in **V** indicating that ν_{14} (b_2) is underestimated by the theoretical computation. Unfortunately, this region of the vibrational spectrum was not measured in refs 24 and 26. (However, it is necessary to note that the assignments of three pairs of frequencies, ν_4 and ν_6, ν_{11} and ν_{12}, and ν_{14} and ν_{15} in this work (Table 5) are inverted compared with the assignments in ref 26.)

In addition, the assignments of two b_1 vibrations, ν_9 and ν_{10}, were in doubt as well.[24] To gain greater insight into which assignment is more reasonable, the vibrational problems were solved with artificial masses for all three carbon atoms and for the F atoms attached to C_1 and C_2. The frequency shifts for these artificial isotopic molecules reveal that the band at 1331 cm^{-1} should be assigned to ν_{10}, the $\nu(C-C)$as.str vibration, and the 892 cm^{-1} band should be assigned to ν_9, the $\nu(=C-F)$-as.str vibration, as in ref 26.

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The calculation results simulate the interesting feature of this spectrum (i.e., that the symmetrical and antisymmetrical rocking vibrations of the $=C-F$ moieties, ν_4 and ν_{11}, are not virtually split). Approximately the same situation is observed for ν_3 and ν_{10}, $\nu(C-C)$str, as well as ν_1 and ν_9, $\nu(=C-F)$str.

A partial refinement of the scale factor set B in Table 3 was carried out, involving only the coordinates responsible for vibrations of the $=C-F$ moieties. Note, however, that only one experimental frequency, 616 cm^{-1}, is available for the χ-$(=C-F)$wag coordinate. The refined set of scale factors obtained is given in Table 3, column C.

The scale factor sets obtained for **I**, **II**, and **V** were used to compile the sets for **III**, **IV**, **VI**, and **VII** (Table 3).

1,3,3-Trifluorocyclopropene (IV) and Its Deuterated Isotopomer. The set of scale factors for correcting the HF/6-311G*//HF/6-311G* force field of **IV** (Table 3, first column A/C) was compiled entirely from the scale factors for the corresponding coordinates of **I** and **V** without any additional refinement. Table 6 contains the experimental and calculated frequencies for **IV**-d_0 and **IV**-d_1. Note that all the predicted vibrational frequencies are in good agreement with the experimental ones. This work corroborates the assignments suggested in ref 21. However, the calculations of the vibrational frequencies performed in ref 21 and based on the "experimental" force field gave too low a value (159 cm^{-1}) for the out-of-plane vibration frequency of the $=C-F$ moiety, ν_{14} ($\chi(=C-F)$wag), found at 204 cm^{-1} in the experimental spectrum.

The assignment of ν_9 ($\nu(=C-F)$str) was in doubt because of large contributions of the $=C-H$ rock, $=C-F$ rock, CF$_2$ wag, and C$-$C stretch coordinates into the form and the PED of this normal mode, which is probably due to the low symmetry of **IV**. To obtain additional evidence in favor of the attribution of the 854 cm^{-1} band to the $\nu(=C-F)$str vibration, calculations with artificial masses instead of the mass of the F atom in the $=C-F$ moiety were performed. Results of these calculations revealed a large increase of this frequency with decreasing mass of the substituent atom, indicating that the assignment of ν_9 is indeed correct.

The ν_9 motion also demonstrates an inverse isotopic shift on passing from **IV**-d_0 to **IV**-d_1 (Table 6). By analogy with **II**, the corresponding curves were constructed for the transition of the calculated frequencies from 854 cm^{-1} (ν_9) and 995 cm^{-1} (ν_{11}) (**IV**-d_0) to 884 and 814 cm^{-1} (**IV**-d_1), respectively. The change in the value of the $\nu(C=C)$str frequency will be discussed further below.

3-Fluorocyclopropene (III) and Its Perdeuterated Isotopomer. Compound **III** is also a molecule that did not require further refinement of the scale factors obtained for **I** and **II**. This conclusion is clear from the frequencies calculated using the HF/6-311G*//HF/6-311G* force field and the scale factors for **I** (Table 7, column A). The set of scale factors used to calculate the frequencies in column A/B in Table 7 includes only one scale factor from the B set, namely that responsible for the C$-$F stretch coordinate (Table 3). Involving other scale factors of the B set results in larger deviations of the theoretical frequencies from the experimental data. The assignments of the ν_4 and ν_8 frequencies are most interesting for the identification of these molecules (fingerprint region). The deviations for the calculated ν_4 and ν_8 frequencies of **III**-d_0 from the experimental ones are about 2% (see Table 7); the deviations may be partially caused by the absence of special scale factors for the $>$CHF moiety. Nevertheless, the values of the ν_4 and ν_8 frequencies for **III**-d_3 are in good agreement with their experimental counterparts.

If the assignments of the IR bands at 1329 and 860 cm^{-1} are beyond doubt, the attribution of the theoretical frequency 906 cm^{-1} (ν_6, Table 7) to the 936 cm^{-1} band of the Raman spectrum in ref 25 is rather questionable (see also footnote to Table 7). Indeed, the IR band at 956 cm^{-1} (ν_{13}) is very strong in the gas phase and overlaps all other bands in this region. However, the IR spectrum in the crystalline phase[25] shows two medium intensity bands at 953 and 914 cm^{-1} and a weak band at 925 cm^{-1}. In ref 25, the first medium intensity band was assigned to ν_{13} (ν(CHF)as.str). The second medium intensity band at 914 cm^{-1} was assigned to an overtone of ν_{14} ($2 \times 457 = 914$). However, it seems more reasonable (taking into account the crystalline shift and anharmonicity) to assign the weak band at 925 cm^{-1} as an overtone of ν_{14}. Hence, in Table 7, the IR band at 914 cm^{-1} is assigned as the experimental counterpart of the theoretical frequency 906 cm^{-1}. This assignment means that the agreement between the calculated and experimental vibrational frequencies of **III**-d_0 and **III**-d_3 is satisfactory, in general.

1,2-Difluorocyclopropene (VI) and 1-Fluorocyclopropene (VII). The scale factor set utilized for correcting the HF/6-311G*//HF/6-311G* force fields were compiled from the scale factor sets of **I** and **V** and is presented in Table 3, column A/C under the notation **VI**−**VII**. The theoretical vibrational frequencies obtained are presented in Table 8. Experimental vibrational spectra of **VI** and **VII** are not available in the literature. Successful predictions of the vibrational spectra of the molecules **III** and **IV** suggest that the predicted vibrational spectra for **VI** and **VII** should be reasonable as well.

Regularities in the Vibrational Spectra of I−V. Juxtaposition of the assigned experimental frequencies of **I**-**V** in Table 9 reveals some special trends in their spectra. First of all, by analyzing the trends in the frequencies due to the three-membered ring in the series **I**-**III**-**II** it is possible to observe the effect of progressively replacing the H atoms at C$_3$ (see Figure 1) by fluorine. The $\nu(C=C)$str frequency (ν_2) undergoes a small decrease whereas the $\nu(C-C)$str frequencies (ν_3 and ν_{10}) increase sharply upon substitution by F at C$_3$ (Table 9). Similarly, the frequencies of the out-of-plane $\chi(=C-H)$wag vibrations (ν_7 and ν_{14}) also increase in the series **I**-**III**-**II**. The shifted frequencies of **III** lie between the corresponding frequencies of **I** and **II**. These shifts are easily explained by changes in values of the scaled force constants (see Tables 11, 12, and 14 in *Supporting Information*). Indeed, the force constants for the $\nu(C=C)$str coordinates in **I**, **III**, and **II** decrease slowly as follows: 10.11, 9.58, and 9.17 mdyn/Å, respectively. For the out-of-plane $\chi(=C-H)$wag coordinates, the force constants in this molecular series are 0.255, 0.276, and 0.285 mdyn × Å, respectively.

The presence of the F atoms attached to C$_3$ also causes measurable decreases in the lengths of the formal single C$-$C bonds (see Table 1). This effect is reflected by changes in the C$-$C bond orders (0.95 and 1.05 in **I** and **II**, respectively) and by the sharp increase in the corresponding force constants in the series **I**-**III**-**II** (viz. 3.84, 4.54, and 5.02 mdyn/Å). Moreover, when going from **I** to **III** and to **II**, the off-diagonal force constants belonging to the C$-$C and CF$_2$ stretch coordinates are enhanced from 0.22 to 0.46 and to 0.64 mdyn/Å, respectively. All these factors bring about the large changes in the C$-$C stretching frequencies and reveal that the electronic structure of the three-membered carbon ring in the region of the formal single C$-$C bonds undergoes an important reconstruction on substitution of the H atoms on C$_3$ by F atoms. This reconstruction will affect the reactivity of the three-membered ring.

Analysis of the spectra of **II**, **IV**, and **V** also makes it possible to observe the effect of substitution of the H atoms at the formal double bond by fluorine. The increase in the $\nu(C=C)$str frequency (ν_2) in the series **II**−**IV**−**V** is the most interesting effect. The increase in the $\nu(C-C)$str. frequency, ν_{10}, in **V** is unusual and unexpected. Increases in the frequencies for the $\chi(CF_2)$wag and $\rho(CF_2)$rock vibrations of the $>CF_2$ moiety are also observed (see ν_{12} and ν_{15} for **II**, **IV**, and **V** in Table 9). All other shifts in the frequencies are typical of those expected when passing to a heavier molecule.

The large increases of ν_2 on going from **II** to **IV** and to **V** is accompanied by a small increases in the corresponding scaled force constants (viz. from 9.17 to 9.73 and to 10.08 mdyn/Å, respectively). An analogous increase of the ν_2 frequencies is observed in the following series: **I**, 1-methyl-**I**, and 1,2-dimethyl-**I**,[13] where the corresponding frequencies are 1653, 1788, and 1890 cm^{-1}, respectively. However, these changes are not accompanied by an increase in the corresponding force constants as calculated at the HF/6-31G*//HF/6-31G* level.[13] In contrast, the scaled diagonal force constants were found to decrease very slowly, being equal to 10.16, 10.06, and 9.99 mdyn/Å, respectively.[13] It was also shown that substitution of the H atoms in positions 1 and 2 by methyl groups causes little change in the formal $C=C$ and $C-C$ bond lengths in the cyclopropene ring. This result indicates that the increase in the $\nu(C=C)$ stretching frequency is not directly connected with the reconstruction of the electronic structure of the $C=C$ bond, which could manifest itself in changes of the $C=C$ and $C-C$ bond lengths in the three-membered rings. This result was also supported by the calculated values of bond orders[31] for all bonds of these molecules. A very small regular decrease was observed only for the $C=C$ bond order for **I**, 1-methyl-**I**, and 1,2-dimethyl-**I**[13]; the values are 1.97, 1.94, and 1.91, respectively. It was shown that this effect is brought about primarily by kinematic factors; that is, by increase of the mass of the molecules upon substitution and by changes in the mutual distribution of the atomic masses.[13]

The rather small increase in the $\nu(C=C)$str force constants in the series **II**-**IV**-**V** makes it possible to suppose that kinematic factors provide the greatest contribution to the effect just mentioned. This conclusion is supported by the solutions of the vibrational problems using masses varied from 1 to 19 for the H atom on C_1 in **II** and masses varied from 19 to 1 for the F atom on C_1 in **IV**. The changes in the frequencies ν_2 and ν_9 for **II** and ν_2 and ν_3 for **IV**, as a function of the hypothetical masses, are represented in Figures 3 and 4, respectively. The scaled force fields of **II** and **IV** were used to calculate all points in Figures 3 and 4, respectively.

As in the case of the inverse isotopic shift (see Figure 2), there are certain points on Figure 3 where the components of the PED's for the $C=C$ and $=C-H$ stretch coordinates, corresponding to the frequencies ν_2 and ν_9, become equal to each other. With a further increase in mass of the hypothetical atom, the contributions of the corresponding coordinates into the PED's get mutually interchanged (Figure 3).

Note that the lower curve in Figure 4 corresponds to the ν-$(C-C)$str vibration instead of the $\nu(=C-F)$str mode. This result is explained by the strong mixing of these two vibrations in **IV**. There are points in Figure 4 where the components of the PED's for the $C=C$ stretch and $C-C$ stretch coordinates are equal. Decreasing the hypothetical mass of the F atom in the $=C-F$ moiety beyond these points results in a change in the assignments of these frequencies. Note that the final calculated values are rather close to the corresponding experimental ones.

The analysis performed confirms the dominant contribution of kinematic factors to the increase in the theoretical frequencies of the $\nu(C=C)$str vibrations in the series **II**-**IV**-**V**. This conclusion is also supported by the calculated values of the bond orders for the formal double bonds in this molecular series; namely, 1.78, 1.71, and 1.66 for **II**, **IV**, and **V**, respectively. However, these decreases are larger than those obtained for **I** and its methyl derivatives.[13]

Conclusions

The refined scale factors obtained for the HF/6-311G*//HF/6-311G* force field of **I**-d_0 allowed rather accurate determination of the force fields of **II**-**V** (see the frequencies in Tables 4−7, columns A). The range of scale factor values for **I** is rather small: from 0.840 to 0.707 for the $C-H$ stretch and the $=C-H$ wag coordinates, respectively. The scale factors refined for **II** and **V** lie in the same range except that for the $=C-F$ wag coordinate, which is 0.655. The similarity of the scale factors for the hydrogenated and fluorinated compounds is obviously explained by the same column position of the fluorine atom with respect to the H atom in the Mendeleev Periodic System of chemical elements; that is, their electronic structures are similar because they require one electron to fill their outer shell.

The joint vibrational quantum mechanical analysis of **I**, **II**, and **V** allowed sufficiently accurate prediction of the theoretical vibrational frequencies for **III** and **IV** and assignment of the experimental frequencies of the molecules **I**−**VII** and their deuterated isotopomers. Some experimental bands of the deuterated isotopomers of **I** and several bands of **III**, **IV**, and **V** are reassigned. The unusual, regular and large increase of the frequencies of the $\nu(C=C)$str bands in the molecular series **II**-**IV**-**V** is corroborated by the analysis performed and explained by kinematic factors. The use of a scaled force field can obviously give additional evidence permitting the discovery of Fermi resonance.

The presence of the two F atoms at C_3 in **II** increases both the force constants and the bond orders of the formal single carbon−carbon bonds and decreases their lengths. Obviously, these changes can affect the reactivity of 3,3-difluoro substituted cyclopropene derivatives.

Examination of the Tables containing the scale factors (Table 3) and the scaled force constants (Tables 11−17 in *Supporting Information*) reveals that the scaled force constants for the quasiequivalent coordinates in the related molecules are somewhat different. However, they give theoretical frequencies that are in good agreement both with the characteristic and non-characteristic experimental frequencies. This result supports the idea of transferability of scale factors rather than the transferability of force constants in this series of related molecules.

Supporting Information Available: Tables with the definition of the coordinates (Table 10) and with the matrixes of the scaled force constants (Tables 11−17) (8 pages). Ordering and accessing information is given on any current masthead page.

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