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Vibrational and Quantum Chemical Studies of 1,2-Difluoroethylenes: Spectra of 1,2-$^{13}C_2H_2F_2$ Species, Scaled Force Fields, and Dipole Derivatives

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Infrared and Raman spectra are reported for cis and trans 1,2-$^{13}C_2H_2F_2$. Quantum chemical calculations at B3LYP and MP2 levels have been made for cis and trans 1,2-difluoroethylenes, using 6-311G** and 6-311++G** bases. The resulting harmonic force fields for each compound were scaled with nine independent factors, using frequency data corrected, where necessary, for Fermi resonances and for liquid/gas shifts. The previously accepted assignments for ν_7 and ν_{12} in the trans isomer are interchanged. Several scale factors for bending motions differ markedly between the cis and trans compounds. Centrifugal distortion constants observed with significant accuracy are predicted within 6%. Harmonic contributions to the vibrational dependence of the rotational constants and perpendicular amplitudes are calculated. The C═C and C−H bonds in the cis and trans isomers are essentially identical in respect to length, force constant, and isolated CH stretching frequency. However, the C−F bond is slightly stronger in the cis compound. A revised allocation of observed infrared intensity between the overlapping trans ν_7 and ν_{12} bands is needed. Directions of $\partial \boldsymbol{p}/\partial Q$ for the trans B_u bands are given, which differ from those reported earlier. Magnitudes and directions of the bond dipole derivatives $\partial \boldsymbol{\mu}/\partial r$ for the CH and CF bonds are obtained from calculated atomic polar tensors. In both cis and trans isomers, the vector $\partial \boldsymbol{\mu}/\partial r_{CF}$ lies within 17° of the bond direction, but for the CH bond, $\partial \boldsymbol{\mu}/\partial r$ is roughly perpendicular to the CH direction.

Introduction

The molecules of *cis*- and *trans*-1,2-difluoroethylene have been the subject of a number of experimental[1−9] and theoretical studies.[10−17] A major interest has been the extent to which parameters of all kinds—bond lengths and angles, force constants, and atomic polar tensors—are transferable from one isomer to the other. However, in each of these areas, significant problems remain.

With respect to geometry, whereas the spectroscopically based cis/trans differences in HCC and FCC angles are well reproduced by ab initio calculations,[4] as seen also in Table 1, the same is not true for the bond lengths. The observed shortening in rC−F of 0.015 Å and the observed lengthening of rC−H and rC═C by 0.008 and 0.009 Å, respectively, on passing from trans to cis have not been confirmed by the ab initio approach.[4]

An independent check on the CH distances may be made by a comparison of the ν^{is}CH values, measured in partially deuterated species, which are known to correlate well with CH distance. A change of 0.008 Å in r_0, for instance, would entail a change in ν^{is}CH of 78 cm^{-1} between the isomers,[18] whereas from the same change in r_e, a $\Delta\nu^{is}$CH value of 111 cm^{-1} would be anticipated.[19] Unfortunately, ethylenic CH stretching bands are notoriously subject to Fermi resonances. An earlier, cursory examination of this region of the spectra of the 1,2-difluoroethylenes yielded a $\Delta\nu^{is}$CH(cis/trans) value of 13 cm^{-1},[20] but a more critical scrutiny of the spectra is overdue.

TABLE 1: Comparison of Calculated and Observed Geometries and Dipole Moments and QC Energies for cis and trans 1,2-Difluoroethylenes

	B3LYP		MP2		
parameter	tz	tz+	tz	tz+	obs[a]
			cis		
rCH/Å	1.08150	1.08098	1.08154	1.08153	1.088(2)
rCC/Å	1.32337	1.32374	1.33114	1.33223	1.325(2)
rCF/Å	1.34227	1.34323	1.33794	1.33922	1.337(2)
∠HCC/deg	122.728	122.98	122.215	122.50	123.9(2)
∠FCC/deg	122.726	122.60	122.673	122.47	122.1(2)
μ/D	2.378	2.592	2.389	2.582	2.42
$-E$/H − 276[b]	1.130042	1.142842	0.477285	0.49291	
			trans		
rCH/Å	1.08175	1.08132	1.08181	1.08193	1.080(2)
rCC/Å	1.32243	1.32230	1.33054	1.33110	1.316(2)
rCF/Å	1.34711	1.35002	1.34258	1.34583	1.352(2)
∠HCC/deg	125.020	125.70	124.593	125.34	126.3(2)
∠FCC/deg	120.341	120.03	120.204	119.80	119.2(2)
$-E$/H − 276[b]	1.129935	1.141565	0.476966	0.49155	
			cis−trans		
ΔrCH/Å	−0.0003	−0.0003	−0.0003	−0.0004	0.008(3)
ΔrCC/Å	0.0009	0.0014	0.0006	0.0011	0.009(3)
ΔrCF/Å	−0.0048	−0.0068	−0.0046	−0.0066	−0.015(3)
Δ∠HCC/deg	−2.29	−2.72	−2.38	−2.83	−2.4(3)
Δ∠FCC/deg	2.39	2.58	2.47	2.67	2.9(3)
ΔE/kcal mol^{-1}	−0.067	−0.802	−0.200	−0.870	−1.09[c]

[a] cis—ref 2, mw; trans—ref 4, r_s/r_0. [b] E = energy in Hartrees. [c] Reference 5.

Problems likewise exist in the area of force constants. The frequency data for the d_0, d_2, and d_1 isotopomers obtained by Craig and Overend were used by these authors[5] and also by Pearce and Levin[11] to calculate force fields. In both papers, it was concluded that the C═C stretching force constant was 5% greater in the cis isomer than in the trans, which is surprising

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in view of the greater length of this bond in the cis. However, both treatments adopted an "overlay" approach, the assumption of some force constants common to both cis and trans isomers; both employed only a limited number of parameters (13 or 17 out of a possible 25) in the in-plane vibrational species, and neither made any attempt to diagnose the presence of Fermi resonances or to allow for changes in frequency upon change of phase.

A third problem area involves the atomic polar tensors (APTs) and related quantities for the two molecules. Theoretical values of APTs are determined directly in standard ab initio programs and thereafter are used to compute the infrared intensities. Experimental values of APTs can be obtained from measured infrared intensities, provided the directions of the dipole derivatives with respect to normal coordinate, $\partial \boldsymbol{p}/\partial Q$, are known. However, the lack of symmetry of the trans isomer with respect to the *a* and *b* rotation axes means that this information cannot be obtained by current techniques from observed spectra in the case of the in-plane vibrations.

This difficulty has been tackled in several ways,[12−15] of which the most satisfactory is to combine ab initio calculations of the directions of $\partial \boldsymbol{p}/\partial Q$ with the experimental intensities.[15] However, there are worrying features in the published calculations. A dramatic change is reported in the direction of $\partial \boldsymbol{p}/\partial Q_9$, for the CH stretching vibration ν_9, from *trans*-1,2-difluoroethylene to *trans*-1,2-dichloroethylene, which must reflect a fundamental difference in the APT for the H atom in the two compounds.[15] This situation is chemically implausible. In addition, all the calculated infrared intensities suggest that the division of experimental infrared intensity made originally[9] between the overlapping bands due to ν_7 and ν_{12} in *trans*-1,2-$C_2H_2F_2$ is seriously wrong.

In the present work, we shed light on these problems by presenting, first, vibrational spectra of ^{13}C-labeled species of both cis and trans isomers[21] and second, new quantum chemical (QC) studies, at the heart of which are scaled general force fields. Together, these new data have enabled a thorough reappraisal of existing spectra to be made, which has resulted in the reassignment of ν_7 and ν_{12} in *trans*-1,2-$C_2H_2F_2$ and the identification of a number of resonances in both compounds.

Spin-offs from the quality force fields that we produce include (1) calculations of the harmonic corrections to the vibrational dependence of the rotational constants and perpendicular amplitudes, which will be required if more sophisticated experimental geometries, such as r_z,[22] are to be obtained; (2) improved normal coordinates needed for more precise interpretations of the experimental infrared intensities; and (3) centrifugal distortion constants for as many isotopomers as may be required.

If a close comparison of force constants in the two isomers is to be made, it is clear that each QC-based force field must be scaled independently of the other. It is also essential to allow independent scaling of the force constants for each type of coordinate within the same molecule. This scaling then provides an opportunity for testing the validity of the overlay principle often applied to scale factors—identical scale factors for the same level of theory for similar motions throughout a series of molecules of similar structure.[23,24] This principle is frequently combined with the assumption of a common scale factor for a group of motions (e.g., HCC or HCH bendings) within any one molecule.[23,24] Prior studies indicate that these assumptions are unwarranted if spectra are to be reproduced closely.[25−27]

In choosing the level of QC calculation to be employed, density functional theory (DFT) methods are currently much favored because they tend to yield calculated vibration frequencies closer to experimental (anharmonic) values, that is, their scale factors are closer to unity than are those from an HF or MP2 approach.[23] Computing times are also shorter than those for a comparable MP2 calculation. However, it is arguable that the value of a given QC approach is as much to be judged by the *spread* of its scale factors as by their approach to unity. A recent example suggests that there is little to choose between DFT and MP2 calculations in this respect,[28] which means that the need for care in scaling is equally great in both types of calculation if the data are to be fitted precisely.

Experimental Section

Samples of *cis*- and *trans*-$^{13}C_2H_2F_2$ were those described before.[4] Gas-phase infrared spectra were recorded with 0.5 cm^{-1} resolution on Perkin-Elmer 1760 (mid-IR) and 1700X (far IR) FTIR instruments. Windows of the 10-cm cells were cesium iodide or polyethylene. Frequencies are good to 0.1 cm^{-1}, but band centers cannot be determined with this accuracy in medium-resolution spectra. Liquid-phase Raman spectra were recorded at about 2.5-cm^{-1} resolution on a Spex Ramalog 5 with excitation by 265 mW of the 514.5-nm line of a Coherent Innova 70 argon ion laser. A Kaiser Optical corner cube filter was used to isolate the laser line. A Nicolet 1180 data system facilitated the data collection. Samples were held in 1.8-mm capillaries in a Harney−Miller-type cold cell suited to 90° geometry. For the cis isomer, the temperature was −62 °C; for the trans isomer, −67 °C. Frequencies are reliable to ±2 cm^{-1} after calibration with atomic lines of argon from a pencil lamp.

In addition to the high-resolution data reported earlier,[3,4,6,7] reexamination of improved infrared spectra of the d_0, d_2, and d_1 isotopomers prompted small adjustments in a few of the experimental frequencies for these species, as listed below in Tables 2 and 3.

Theoretical Section

Ab initio and DFT calculations were carried out using the program Gaussian 94.[29] Optimization and force constant calculations were made throughout the series at two levels of theory, MP2 and B3LYP,[30−32] each with two basis sets: 6-311G**, hereafter "tz", and 6-311++G**, hereafter "tz+". Inclusion of diffuse functions is important if the additional stability of the cis compound is to be satisfactorily reproduced in the theoretical calculation.[10] In all cases, the "tight" condition for optimization in the Gaussian input was employed. Also, to improve the precision of the B3LYP calculations, a fine grid was employed consisting of 99 radial shells around each atom and 302 angular points in each shell. Under these conditions, bond lengths were reproducible to 0.00005 Å or better. Four decimal place precision is desirable because it helps to avoid the rather large rounding errors in small differences such as those found between the cis and trans compounds, which otherwise occur if the custom of rounding off ab initio bond lengths to ±0.001 Å is followed. Moreover, a rounding error in r_eC−H of 0.001 Å corresponds to a change in ν^{is}CH of about 14 cm^{-1},[19] which is undesirable in any discussion of CH stretching frequencies.

For the calculation of the force field in internal coordinates and subsequent scaling, the QC output of Cartesian force constants and atomic coordinates was input into the program ASYM40,[33] which scales force constants in symmetry coordinate space according to the procedure recommended by Pulay et al.[34] Off-diagonal constants are multiplied by the geometric mean of the scale factors associated with the corresponding two

TABLE 2: Unscaled and Scaled Frequencies (cm^{-1}), Unscaled IR Intensities, and Frequency Fit for cis 1,2-Difluoroethylenes

A. d_0

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		$\nu_{un}{}^a$	A^b	$\nu_{un}{}^a$	A^b	$\nu_{obs}{}^c$	$\sigma_\nu{}^d$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$
A_1	1	3238.5	6	3295.9	6	3122	31.2	0.0	0.1	−0.1	0.1
	2	1755.8	61	1762.7	62	1712^f	17.1	−3.1	−2.3	−4.9	−4.3
	3	1280.1	41	1297.3	40	1263.7	12.6	−6.0	−8.7	−5.0	−7.2
	4	1009.4	77	1021.2	70	1009^f	10.1	2.4	1.5	8.3	7.8
	5	236.2	2	238.2	2	236.8	2.4	0.3	0.4	0.3	0.3
A_2	6	868.7		847.8		833	8.3	−0.2	0.3	−1.2	−1.0
	7	509.3		506.8		495^g	∞	−5.5	−7.8	−1.7	−2.4
B_1	8	3215.7	5	3271.8	6	3137.1	∞	37.8	37.3	38.9	38.7
	9	1381.4	29	1401.7	32	1374^f	13.7	0.8	4.2	−0.8	1.7
	10	1124.1	145	1154.3	126	1131.2	11.3	−0.5	−0.9	−5.9	−6.5
	11	770.5	33	775.4	31	769.8	7.7	−0.3	−0.2	0.0	0.1
B_2	12	774.5	55	785.5	52	756.4	7.6	−1.0	−0.3	−2.0	−2.0

B. d_0 ($^{13}C_2$)

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		$\nu_{un}{}^a$	A^b	$\nu_{un}{}^a$	A^b	$\nu_{obs}{}^c$	$\Delta\nu_{obs}{}^h$	$\Delta\nu_{sc}{}^h$	$\Delta\nu_{sc}{}^h$	$\Delta\nu_{sc}{}^h$	$\Delta\nu_{sc}{}^h$
A_1	1	3226.8	6	3283.9	5	3109	13	11.3	11.4	11.4	11.5
	2	1692.9	56	1699.9	57	1652^f	60^f	60.7	60.9	60.7	60.9
	3	1276.1	40	1292.9	39	1257.5	6	4.6	4.6	4.5	4.4
	4	991.2	75	1002.7	68	995.9	20	18.2	18.1	18.2	18.1
	5	235.4	2	237.4	2	236.4	0	0.8	0.8	0.8	0.8
A_2	6	860.9		841.3		828	7	7.2	7.7	6.3	6.4
	7	496.2		493.2		485^g	13	13.1	12.8	13.5	13.4
B_1	8	3206.0	5	3261.9	6	3110.7	26.4	9.4	9.4	9.4	9.5
	9	1367.5	19	1386.5	22	1360	16	15.5	14.6	16.2	15.2
	10	1103.0	149	1133.8	131	1112.2	19	19.7	20.4	19.3	20.1
	11	751.3	29	756.0	28	751	19	19.3	19.3	19.2	19.2
B_2	12	768.2	56	779.1	52	750	6	6.1	6.1	6.2	6.2

C. d_2

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		$\nu_{un}{}^a$	A^b	$\nu_{un}{}^a$	A^b	$\nu_{obs}{}^c$	$\sigma_\nu{}^d$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$
A_1	1	2414.3	3	2455.4	4	2323^i	∞	−4.5	−5.2	−5.1	−6.1
	2	1715.1	80	1725.4	80	1676	16.8	0.1	0.6	−3.3	−2.8
	3	1060.7	93	1077.4	85	1060^f	10.6	−1.4	−3.8	4.5	1.9
	4	856.6	7	863.7	7	847	8.5	0.4	0.4	2.0	2.9
	5	234.5	2	236.3	2	234	2.3	−0.7	−0.7	−0.6	−0.6
A_2	6	704.6		678.9		678^g	∞	3.7	−1.5	12.0	10.4
	7	452.2		455.7		445^g	∞	−0.3	1.3	−2.9	−2.4
B_1	8	2368.0	5	2409.6	6	2284^i	∞	0.9	0.4	1.0	0.8
	9	1207.3	151	1238.8	142	1221	12.2	1.8	9.3	−5.3	2.2
	10	944.8	24	959.6	17	940	9.4	3.4	−0.1	3.3	−1.0
	11	749.1	30	753.7	28	749	7.5	0.9	0.7	1.3	1.1
B_2	12	608.6	25	617.6	23	596	6.0	0.6	1.3	−0.7	−0.3

D. d_1

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		$\nu_{un}{}^a$	A^b	$\nu_{un}{}^a$	A^b	$\nu_{obs}{}^c$	$\sigma_\nu{}^d$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$	$\epsilon_\nu{}^e$
A'	1	3227.3	6	3284.1	6	3123	∞	12.2	12.0	12.6	12.6
	2	2391.5	4	2432.7	5	2305^i	∞	−0.7	−1.3	−0.9	−1.5
	3	1735.0	71	1743.7	71	1696	17.0	1.0	1.7	−1.6	−1.1
	4	1340.9	38	1360.6	41	1330	13.3	−3.1	−0.7	−4.7	−2.5
	5	1161.9	143	1191.0	128	1168	11.7	−1.9	−0.5	−6.2	−4.7
	6	1033.4	92	1050.1	82	1034	10.3	0.8	−1.7	5.5	2.7
	7	897.1	11	906.3	9	890	8.9	2.4	1.7	3.4	3.2
	8	758.7	32	763.4	30	757	7.6	−0.8	−1.0	−0.3	−0.5
	9	235.4	2	237.3	2	236	2.4	0.4	0.4	0.4	0.4
A''	10	831.7	19	820.4	21	802	8.0	0.2	0.2	0.0	0.0
	11	650.3	21	646.7	16	632	6.3	0.3	−1.9	3.9	3.2
	12	477.5	0	479.6	0	470	0.0	0.0	0.3	−0.4	−0.3

[a] Unscaled frequency (cm^{-1}) from the QC calculation. [b] Infrared intensity in km mol^{-1}. [c] This work or ref 5, from the gas phase except where otherwise indicated. Values quoted to 0.1 cm^{-1} were obtained with resolution superior to that in ref 5. [d] Uncertainty. ASYM40 assigns each datum the weight σ^{-2}.[33] [e] $\nu_{obsd} - \nu_{scaled}$ (cm^{-1}). [f] Corrected for Fermi resonance. [g] Liquid-phase value. [h] $\nu(^{12}C_2) - \nu(^{13}C_2)$. Observed values are based on comparable spectra before rounding off. [i] Observed value/1.011 (correction for difference in νCH and νCD anharmonicity).

TABLE 3: Unscaled and Scaled Frequencies (cm^{-1}), Unscaled IR Intensities, and Frequency Fit for trans 1,2-Difluoroethylenes

A. d_0

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		ν_{un}[a]	A[b]	ν_{un}[a]	A[b]	ν_{obs}[c]	σ_ν[d]	ϵ_ν[e]	ϵ_ν[e]	ϵ_ν[e]	ϵ_ν[e]
A_g	1	3228.9		3285.6		3109[j]	31.1	0.1	−0.2	−0.8	−1.1
	2	1741.3		1745.5		1702[j]	17.0	−0.2	0.2	−0.3	0.1
	3	1302.6		1317.8		1286[g]	20.0	5.1	1.6	5.9	2.4
	4	1132.0		1155.1		1123[g]	∞	−19.2	−17.9	−19.4	−17.2
	5	551.2		556.1		552[j]	5.5	0.7	0.5	1.0	0.6
A_u	6	903.8	83	911.8	80	874.2	8.8	−2.3	−2.1	−2.4	−2.0
	7	334.1	5	339.7	5	335	3.4	1.0	0.9	1.0	0.8
B_g	8	823.8		809.2		788[g]	20.0	0.4	0.1	0.0	−0.3
B_u	9	3221.7	14	3277.4	14	3101[f]	31.0	−0.1	0.1	0.7	0.9
	10	1286.1	10	1307.9	17	1274.2	12.7	−2.3	0.9	−4.4	−0.7
	11	1148.8	351	1182.2	319	1159[f]	11.6	−2.3	−4.7	−0.6	−3.7
	12	317.4	14	318.0	14	324	3.2	−2.7	−2.4	−2.9	−2.6

B. d_0 ($^{13}C_2$)

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		ν_{un}[a]	A[b]	ν_{un}[a]	A[b]	ν_{obs}[c]	$\Delta\nu_{obs}$[h]	$\Delta\nu_{sc}$[h]	$\Delta\nu_{sc}$[h]	$\Delta\nu_{sc}$[h]	$\Delta\nu_{sc}$[h]
A_g	1	3217.0		3273.4		3096[g]	15	11.4	11.6	11.6	11.8
	2	1680.4		1685.1		1637[g]	57	58.5	58.8	58.6	58.9
	3	1294.0		1309.3		1276[g]	10	8.9	8.7	8.7	8.5
	4	1104.8		1126.9		1092[f,g]	31[f]	27.7	27.6	28.0	27.8
	5	547.5		552.3		545[g]	3	3.7	3.8	3.6	3.7
A_u	6	900.9	84	908.9	80	870	4	2.8	2.8	2.8	2.9
	7	327.0	5	332.5	5	326	9	7.1	7.1	7.1	7.1
B_g	8	807.9		793.7		775[g]	13	15.3	15.2	15.2	15.1
B_u	9	3212.0	13	3267.5	13	3103.4	12.8	9.4	9.4	9.4	9.4
	10	1279.2	4	1299.9	7	1266.0	8.2	8.6	8.7	9.5	8.2
	11	1124.3	341	1157.7	314	1139.0	23	23.5	24.4	22.7	23.7
	12	311.3	13	311.9	14	318	6	6.2	6.3	6.2	6.2

C. d_2

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		ν_{un}[a]	A[b]	ν_{un}[a]	A[b]	ν_{obs}[c]	σ_ν[d]	ϵ_ν[e]	ϵ_ν[e]	ϵ_ν[e]	ϵ_ν[e]
A_g	1	2416.4		2456.4		2329[i]	∞	2.7	0.0	1.0	−1.9
	2	1687.8		1695.0		1650[f,j]	∞	−0.6	0.5	−2.6	−1.3
	3	1120.1		1136.3		1109[g]	∞	−13.0	−12.7	−11.4	−10.5
	4	942.2		957.6		935[g]	20.0	2.0	0.0	3.7	1.7
	5	540.8		545.9		541[j]	5.5	0.1	0.3	−0.3	−0.1
A_u	6	667.9	39	674.1	37	650.0	6.5	2.1	1.9	2.2	1.8
	7	324.8	6	330.1	6	324	3.2	−0.6	−0.6	−0.7	−0.5
B_g	8	716.2		702.8		685[g]	20.0	0.0	0.1	0.2	0.3
B_u	9	2367.8	17	2409.4	16	2286.3[i]	∞	5.8	6.1	6.1	6.2
	10	1159.0	338	1194.4	317	1176.4	11.8	0.8	3.4	−1.6	1.6
	11	949.8	18	964.9	15	943.1	9.4	1.2	0.9	3.0	1.2
	12	299.1	12	299.6	13	309	3.1	2.0	1.7	2.1	1.9

D. d_1

		B3LYP/tz+		MP2/tz+				B3LYP		MP2	
								tz	tz+	tz	tz+
mode		ν_{un}[a]	A[b]	ν_{un}[a]	A[b]	ν_{obs}[c]	σ_ν[d]	ϵ_ν[e]	ϵ_ν[e]	ϵ_ν[e]	ϵ_ν[e]
A′	1	3225.4	7	3281.6	7	3110.6	∞	5.0	5.0	5.0	5.0
	2	2392.8	8	2433.5	8	2311.3[i]	∞	7.3	6.0	6.4	5.1
	3	1714.9	0	1720.7	0	1674	∞	−2.9	−2.0	−3.8	−2.9
	4	1289.0	7	1307.9	12	1270[f]	12.7	−3.6	−3.5	−4.8	−4.2
	5	1153.2	335	1186.9	317	1167.6	11.7	0.8	0.5	1.0	0.4
	6	1130.4	9	1150.1	2	1138	11.4	1.4	2.2	2.0	3.6
	7	947.4	9	962.8	7	940.4	9.4	1.1	0.1	2.3	1.1
	8	546.1	0	551.1	0	545[j]	5.4	−1.2	−1.2	−1.2	−1.3
	9	307.7	13	308.2	13	317	3.2	0.8	0.8	0.8	0.8
A″	10	859.4	42	857.9	44	827.6	8.3	−0.9	−1.0	−1.1	−1.2
	11	698.7	19	693.3	15	672.6	6.7	0.4	0.5	0.6	0.6
	12	330.4	6	335.9	6	330	3.3	−0.3	−0.3	−0.3	−0.3

[a] Unscaled frequency (cm^{-1}) from the QC calculation. [b] Infrared intensity in km mol^{-1}. [c] This work or ref 5, from the gas phase except where otherwise indicated. Values quoted to 0.1 cm^{-1} were obtained with resolution superior to that in ref 5. [d] Uncertainty. ASYM40 assigns each datum the weight σ^{-2}.[33] [e] $\nu_{obsd} - \nu_{scaled}$ (cm^{-1}). [f] Corrected for Fermi resonance. [g] Liquid-phase value. [h] $\nu(^{12}C_2) - \nu(^{13}C_2)$. Observed values are based on comparable spectra before rounding off. [i] Observed value/1.011 (correction for difference in νCH and νCD anharmonicity). [j] Gas−liquid correction applied.

diagonal constants. However, there seems to be no sound justification for this procedure, and instances of a need to refine off-diagonal constants separately are not uncommon.[35−37]

In carrying out the scaling, a decision has to be made as to whether corrections for anharmonicity should first be made to the observed frequency data employed. Normally, such corrections are omitted, and the anharmonicity is incorporated into the scale factor, which can be unfortunate when the effects of anharmonicity are rather different in different isotopomers, such as those involving hydrogen and deuterium. The situation is most acute in treating CH and CD stretching frequencies where the respective anharmonicities are about 4 and 2.6%. A palliative measure that has been found to be effective in many compounds is to divide observed νCD values by 1.011, for fitting in a refinement that employs observed νCH values.[38] This empirical factor of 1.011 is a consequence of Dennison's rule[39,40] and proves to be useful with these fluoroethylenes. A general allowance for anharmonicity is implicit in the uncertainties input in connection with the frequency data. As shown in Tables 2 and 3, these uncertainties were set at 1% except where the data were more doubtful.

Another issue is whether centrifugal distortion data should be included in the scale factor refinement. The distortion constants depend on the geometry of the molecule and on the totally symmetric part of the force field. As obtained from the ASYM40 program, the values of the constants will reflect the QC geometry involved and will apply to the equilibrium state, whereas experimental values are normally determined for the ground vibrational state. Differences between these quantities may amount to 5−10%.[41] In ethylene, for example, where the experimental accuracy is better than 0.1%, differences between experimental values and those derived from high-level theory lie in the range 2−6%.[42] Caution is therefore needed here.

A similar issue concerns the use of the $^{13}C_2$ frequency shifts. These reflect the carbon atom amplitudes in the various modes and are valuable in a refinement in circumstances where the shift is known precisely, preferably ±0.1 cm^{-1}, and where there is no effect of Fermi resonance or an abnormal effect of anharmonicity.[43] Because these conditions are not met in almost all the data here, we have not used the ^{13}C data in the scaling exercise. However, as shown below, they prove invaluable in the discussion of Fermi resonances, and their excellent reproduction by our scaled force fields indicates that our calculated normal coordinates are quite satisfactory.

Results and Discussion

A complete listing of the frequencies and assignments of infrared (gas phase) and Raman (liquid phase) bands from the $^{13}C_2$-labeled cis and trans compounds is given in Tables 1S and 2S in the Supporting Information. However, frequencies of the fundamental bands from these and the other isotopomers are included in Tables 2 and 3, after correction for Fermi resonance shifts in some instances. Table 1 compares the theoretical values of the geometric parameters obtained in this work for the cis and trans compound with the experimental values. Unscaled frequencies and infrared intensities for the two tz+ calculations are included in Tables 2 and 3.

Geometry. The energy data in Table 1 show the improvement made in the relative stability of the two compounds by the introduction of diffuse functions. Without these, the energies of the cis and trans compounds are essentially identical at the B3LYP level. With the MP2 approach, the cis rotamer is lower in energy by only 0.20 kcal mol^{-1}. However, with diffuse functions present, the additional stability of the cis (0.80 kcal mol^{-1}, B3LYP; 0.87 kcal mol^{-1}, MP2) is close to the experimental value of 1.09 kcal mol^{-1}, a result similar to that previously obtained by Wiberg et al. in an MP2/6-311++G** calculation for a geometry derived from a smaller basis set.[10]

TABLE 4: Unscaled QC (6-311++G) and Observed νCH and νCD Splittings (cm^{-1}) in 1,2-Difluoroethylenes**

	cis d_0	cis d_2	trans d_0	trans d_2
$(\nu_s - \nu_{as})$ (B3LYP)[a]	22.8	46.3	7.2	48.6
$(\nu_s - \nu_{as})$ (B3LYP, f')[b]	5.8	4.2	0.5	0.4
f'/aJ Å^{-2} (B3LYP)	0.0102		−0.0010	
$(\nu_s - \nu_{as})$ (MP2)[a]	24.1	45.8	8.2	47.0
$(\nu_s - \nu_{as})$ (MP2, f')[b]	5.4	4.0	−0.5	−0.3
f'/aJ Å^{-2} (MP2)	0.0098		−0.0008	
$\nu_s - \nu_{as}$ (obs)	−15.1	40	−5[c]	44[c]

[a] Unscaled value of $(\nu_1 - \nu_8)$ (cis) or $(\nu_1 - \nu_9)$ (trans). [b] Contribution to $(\nu_s - \nu_{as})$ from f'. [c] Based on ν_1 (liquid) and ν_9 (gas).

The B3LYP and MP2 treatments agree on the differences between the cis and trans parameters and also on the way that these are affected by the introduction of diffuse functions. Whereas the *r*C−H difference remains unchanged and essentially zero, the longer C═C bond is slightly lengthened and the shorter C−F bond is slightly shortened in the cis compound as it passes from the tz to the tz+ basis. The same is true of the smaller HCC and larger FCC angles in the cis. The disagreement noted earlier[4] between theoretical and experimental values of the bond length differences is very evident with both basis sets.

The increase in the calculated dipole moment in the cis with the inclusion of diffuse functions is a normal feature of such calculations, as in recent calculations for CH_3F and CH_2F_2.[44,45] The better agreement with the observed value from the smaller basis set has been attributed to an accidental cancellation of errors.[44]

Interpretation of Spectra: Frequencies. If meaningful comparisons of force constant, scale factor, or ν^{is}CH are to be made between the cis and trans isomers, then the data used must be free of errors of assignment, Fermi resonances, and the effects of change of phase. The latter give rise to difficulty mainly in the trans compound where frequency data for the A_g and B_g classes are available only from liquid-phase Raman spectra. Each frequency region will be considered in turn.

νCH/νCD Regions. The effects of change of phase on νCH or νCD values appear to be variable, judging by the data reported by Craig and Overend.[5] Changes from gas to liquid are found to vary from about −2 cm^{-1} (trans d_1,ν_2) to +15 cm^{-1} (cis d_2, ν_1). The large upward shifts of around 40 cm^{-1} found in fluoroethanes[24,25] do not appear in these fluoroethylenes. However, it remains advisable to use only gas-phase data as far as possible.

The assessment of Fermi resonance is assisted by the QC calculations in three ways. The most valuable of these is the prediction of the splitting between symmetric and antisymmetric stretching frequencies. These splittings are shown in Table 4 using data from the unscaled tz+ force fields. Unlike the case of CH_3 or CH_2 groups, the splitting here derives almost wholly from the coupling to νC═C stretching motion that is present in the A_g or A_1 modes and absent in the B_u or B_1 vibrations. The νCH/νCH stretch−stretch interaction constant f' makes a contribution that is small in the cis compound and negligible in the trans, as also shown in Table 4.[46] The important result is that ν_1 in the cis compound should lie about 23 (νCH) or 46 cm^{-1} (νCD) above ν_8, whereas the corresponding values for ν_1 and ν_9 in the trans are ∼7 and ∼49 cm^{-1}. Because the observed order of frequencies is the opposite of that calculated in both the cis d_0 and trans d_0 compounds, it is immediately apparent that one or both of the bands concerned is subject to a substantial resonance shift. By contrast, the splittings observed in the d_2 species are much closer to those predicted, ~40 cm^{-1} in the cis and ~44 cm^{-1} in the trans compound.

The second piece of useful information from the QC calculation is the $^{13}C_2$ shift, which is listed in Tables 2 and 3. The predicted shift of 9.4 cm^{-1} for ν_8 in the cis d_0 compound is so much lower than that observed, 26.4 cm^{-1}, that there can be no doubt of a substantial resonance here. A dominant source of resonance in the νCH region of ethylenes is the combination level νC=C + δCH,[47] and this level occurs for the cis d_0 species at 3051 cm^{-1}.[5] A likely estimate of its unperturbed position is $1716 + 1374 - 10 = 3080$ cm^{-1}, after allowing 10 cm^{-1} for a normal effect of anharmonicity. Such a resonance will be markedly reduced in the $^{13}C_2$ species because of the large shift in ν_2, a difference that accounts for the unusually large ^{13}C shift observed on ν_8. Analysis of the $^{13}C_2$ spectra of the cis isomer is complicated by the further close resonance involving ν_2 with $2\nu_6$, but the same resonance involving ν_8 is undoubtedly present (see Table 1S). By contrast, the ^{13}C shift of 13 cm^{-1} observed for ν_1, seen at 3122 cm^{-1} for the d_0 species, agrees within the experimental error with the scaled predicted value of 11.4 cm^{-1} in Table 2, suggesting no Fermi resonance. Scaling the cis νCH force constant to this value for ν_1 then shows good compatibility with νCD values in both d_2 and d_1, provided the latter are first reduced by 1.011. ν_8 is then predicted to occur at ~3099 (d_0) and ~3090 cm^{-1}($^{13}C_2$), implying resonance shifts of ~38 and ~21 cm^{-1}, respectively, which are both plausible.

The same refinement places ν_1 in cis d_1 at ~3111 cm^{-1}, which implies a small resonance shift of ~12 cm^{-1} on the band seen at 3123 cm^{-1}. This revised ν_1 value fits in well with the position observed for the νC=C + δCH level seen at 3005 cm^{-1} (expected value $1696 + 1330 - 10 = 3016$ cm^{-1}).

In the trans d_0 compound, there is no evidence of resonance on ν_1, whose liquid-phase value of 3111 cm^{-1} may be only 2 cm^{-1} greater than the gas-phase value judging by the behavior of ν_1 in d_1. However, ν_9 at 3116.2 cm^{-1} is clearly in resonance with $\nu_2 + \nu_{10}$, which is expected at about $1702 + 1274 - 10 = 2966$ cm^{-1} and seen at 2952 cm^{-1}.[5] (A gas-phase shift of 8 cm^{-1} has been applied to the value of ν_2; see below.) Refining to the corrected values of ν_1 and ν_9 of 3109 and 3102 cm^{-1}, respectively, reproduces $\nu_1(d_2)$ well and yields 5−6 cm^{-1} errors on $\nu_9(d_2)$, ν_1, and ν_2 (d_1), which may indicate residual resonances on these last two bands. The unperturbed value of $\nu_1(d_1)$ is then 3106 cm^{-1}.

The third piece of evidence from the QC calculations concerns the relative values of ν^{is}CH (ν_1 in the d_1 species) in the cis and trans compounds. In keeping with the virtual identity of their respective bond lengths, the two unscaled ν^{is}CH values are predicted (Tables 2 and 3) to lie within ~2 cm^{-1} of each other, with cis > trans. This difference is only 3 cm^{-1} less than that derived from the above estimates of Fermi resonance, which is well within the likely error of the latter. Whereas the normal close connection between the C−H bond length and the ν^{is}CH value breaks down in the fluoroethanes when the number of substituted fluorines is varied,[25] the present pair of compounds is so similar that it would be surprising if any mutual breakdown of the rCH/ν^{is}CH correlation occurred here.

We can now argue that we have both experimental and theoretical evidence for almost identical C−H bond lengths in the cis and trans compounds, compared with the 0.008(3) Å difference derived from the high-resolution experiments.[2−4] It is inconceivable that the observed spectra could be reconciled with a $\Delta\nu^{is}$CH value of 111 cm^{-1}, which 0.008 Å would imply.[19] We therefore have one more instance of the apparent lack of physical significance of C−H distances derived from an r_s structure.[38,18] It would be interesting to know if the same difference in rCH occurred in an r_z structure that was derived with the appropriate isotopic dependence of the bond lengths, as has been done for ethylene.[22]

νC=C Region. In the cis d_0 compound, ν_2 at 1718.1 cm^{-1} is evidently in resonance with $2\nu_6$ at 1659.4 cm^{-1} (expected value $2 \times 833 = 1666$ cm^{-1}). The resonance is enhanced in the $^{13}C_2$ isotopomer where the two bands are at 1670.0 and 1633.9 cm^{-1}, respectively. This enhancement arises because the $^{13}C_2$ shifts expected on ν_2 and $2\nu_6$ are −61 and −14 cm^{-1}, respectively, bringing ν_2 and $2\nu_6$ closer together. Because ν_6 ($^{13}C_2$) is seen weakly in the gas-phase IR spectrum at 827.5 cm^{-1}, the unperturbed values $2\nu^0_6$ and ν^0_2 probably coincide, which would correspond to a W_{266} Fermi resonance parameter of 18.05 cm^{-1}. Transferring this value to the ^{12}C compound then places ν^0_2 at 1711.9 cm^{-1}. The unperturbed $^{13}C_2$ isotope shift on ν_2 then becomes 60.0 cm^{-1}. A 2-cm^{-1} value for $\nu^0_2 - 2\nu^0_6(^{13}C_2)$ would reduce this shift to 59.0 cm^{-1}, leaving $\nu^0_2(^{12}C_2)$ unaffected. The ν_2 bands in the d_2 and d_1 isotopomers appear to be free of resonance.

In the trans compound, a correction must be applied to the Raman liquid frequency of 1694 cm^{-1} in the d_0 species. Comparison of the gas- and liquid-phase data for the cis compound suggests that an increase of about 8 cm^{-1} is appropriate. There is no evidence for resonance. The weak satellite seen at 1666 cm^{-1} occurs at the position expected for the $^{13}C^{12}CH_2F_2$ natural abundance isotopomer.[5]

In the d_2 species, however, two Raman bands at 1655 and 1642 cm^{-1} indicate that substantial resonance affects ν_2 here. This resonance may involve not only $\nu_3 + \nu_5$, as previously suggested,[5] but also $3\nu_5$ because ν_3 at 1109 cm^{-1} and $2\nu_5$ at 1078 cm^{-1} are also likely to be a resonating pair. (The potential constant k_{355} will produce a larger matrix element W at the $3\nu_5$ level.[48]) The calculated deuteration shift $d_0 - d_2$ of about 52 cm^{-1} means that the likely unperturbed position of ν_2 in d_2 is at 1642 cm^{-1} in the liquid phase, which would be feasible only if a third, unobserved level lay below the two observed ones.

The calculated $d_0 - d_1$ shift on the νC=C band of about 26 cm^{-1} is at variance with the 20 cm^{-1} shift seen in the Raman spectra, which suggests that a small resonance occurs also in the d_1 isotopomer involving ν_3 and $2\nu_{10}$ below. A reinspection of this region in d_1 shows the 1674 cm^{-1} band to be unduly wide, which is consistent with this idea. The combination of the absence of gas-phase data with the presence of likely resonances leads us to omit both d_1 and d_2 values of νC=C from the trans scaling refinement.

1400−600 cm^{-1} Region. In the cis d_0 compound, there is a resonance between ν_9 at 1375.3 cm^{-1} and $\nu_5 + \nu_{10}$ at 1366.2 cm^{-1} and another between ν_4 at 1016.0 cm^{-1} and $2\nu_7$ at 988.9 cm^{-1}. The former resonance was considered to be weak with a shift of ~1 cm^{-1},[49] but the latter one was more significant with a W_{477} value of about 11.5 cm^{-1} derived from the liquid-phase data, assuming exact concidence, which puts ν^0_4 at about 1009 cm^{-1} in the gas phase.

In the trans compound, the liquid-phase values of ν_3 and ν_4 in the d_0 and d_2 species were either ignored altogether or given greater uncertainty in the refinement. Phase shifts on νCF modes in fluoroethanes can exceed 20 cm^{-1}.[25] (The error vector in Table 3 suggests that the shift on ν_4 is about 19 cm^{-1}.) Refinement of the relevant scale factors therefore depended on the gas-phase data from the d_1 species.

A possible resonance in the trans d_0 isotopomer is between $\nu_{11}(b_u)$ at 1162.0 cm^{-1} and a band at 1117 cm^{-1} that was previously assigned to the combination $\nu_7 + \nu_8(B_u)$. The reassignment of ν_7 to 335 cm^{-1}, discussed below, places the expected value of $\nu_7 + \nu_8$ at $788 + 335 = 1123$ cm^{-1}. A shift of 3 cm^{-1} in ν_{11} seems adequate. The $^{13}C_2$ shifts are insensitive to any resonance occurring here.

Another resonance may occur with ν_4 in the trans d_1 isotopomer, seen at 1274.3 cm^{-1} in the IR spectrum, involving a band at 1246 cm^{-1} from below. The latter must arise from the level $\nu_7 + \nu_9$ (A′), which is expected at $317 + 940.4 = 1257$ cm^{-1}. However, because there is no sign of Raman intensity near 1240 cm^{-1} and because there is another A′ band in the IR from above at 1341 cm^{-1}, which would have the effect of depressing ν_4, we feel that any resonance on ν_4 must be small, and we choose 1270 cm^{-1} for its unperturbed value.

Region below 600 cm^{-1} (trans). A minor change here involves a liquid−gas shift on ν_5 for trans d_0. A 4-cm^{-1} correction was applied to the liquid-phase value of 548 cm^{-1} on the basis of the interpretation of weak infrared bands at 610 and 723 cm^{-1} because of the differences $1161(b_u) - 552(a_g)$ and $1274(b_u) - 552(a_g)$. A similar shift of 3 cm^{-1} was then added to the corresponding liquid-phase bands in the d_2 (538 cm^{-1}) and d_1 (542 cm^{-1}) species.

A major change in this region is the interchange of the previously accepted assignments for $\nu_7(a_u)$ and $\nu_{12}(b_u)$ in both the d_0 and d_2 isotopomers. In each of these pairs of overlapping infrared bands, we place ν_7 above ν_{12}. In the same way, $\nu_{12}(a'')$ in the d_1 species has to be placed at 332 cm^{-1}, above $\nu_9(a')$ at 316 cm^{-1}. The need for these inversions is indicated first by the unscaled B3LYP and MP2 frequencies in Table 3 that both place ν_7 above ν_{12}. Attempts to scale to the original assignments resulted in very poor fits involving unacceptably large or small scale factors. Second, the scaled calculated frequency shifts from d_0 to d_2, 9.5 and 19.6 cm^{-1} for the A_u and B_u modes, respectively, exactly reproduce those observed in the Xe matrix, which are 9 and 20 cm^{-1}, respectively, for the higher and lower bands.[5] $\nu_7(a_u)$ therefore has to lie above $\nu_{12}(b_u)$.[50]

This leaves the problem for all three species of explaining the apparent C-type contour associated with a band predominantly from a mode of $B_u(d_0, d_2)$ or $A'(d_1)$ symmetry. This contour is the result of the strong second-order Coriolis interaction discussed earlier[5] that is present between the two bands concerned in all three cases. The different intensities of the Q-branch lines of the rotational structure seen above and below the distorted band support the reassignment of the two fundamentals. Consistent with the calculated intensities (Table 3), the lines on the high-frequency side are distinctly weaker than the lines on the low-frequency side. As reported before, the spacing of these lines is about twice the $2A - (B + C)$ spacing of unperturbed Q branches.[4] In our new far-IR spectra of the various trans species obtained with 0.5-cm^{-1} resolution, these Q-branch lines were seen more clearly than before.

Scaling of the Force Fields. The symmetry coordinates used are listed in Table 5. We have a slight preference for our choice of in-plane bending coordinates. Except for a change of sign, these resemble those of Pearce and Levin[11] but differ from those of Kagel et al.[8,9] Compared with the latter, in the d_0 isotopomers ours yield more pure CH bending motions for the frequencies around 1300 cm^{-1} as well as simpler descriptions of the modes in the 500−800 cm^{-1} region. Overall, the off-diagonal terms in the potential energy distributions (PED) are smaller with our coordinates than with those used previously.[8,9]

TABLE 5: Symmetry Coordinates (*S*) for cis and trans 1,2-Difluoroethylenes

		trans		cis	
type	coordinate[a]	A_g (+)	B_u (−)	A_1 (+)	B_1 (−)
νCH	$r_{14} \pm r_{26}$	S_1	S_9	S_1	S_8
νCF	$r_{13} \pm r_{25}$	S_2	S_{10}	S_2	S_9
νCC	r_{12}	S_3		S_3	
$\delta_{\parallel}$CH	$(\alpha_{214} - \alpha_{213}) \pm (\alpha_{126} - \alpha_{526})$	S_4	S_{11}	S_4	S_{10}
$\delta_{\parallel}$CF	$\alpha_{213} \pm \alpha_{125}$	S_5	S_{12}	S_5	S_{11}
$\delta_{\perp}$CH	τ_{4126}		A_u S_6		A_2 S_6
$\delta_{\perp}$CF	τ_{3125}		S_7		S_7
w_{skel}	$w_{1432} + w_{2651}$ (t) or w_{2615} (c)		B_g S_8		B_2 S_{12}

[a] Indices denote atom numbers as in H(4)F(3)C(1)═C(2)H(6)F(5). τ and w denote dihedral and out-of-plane bending angles, respectively. B elements for the latter are calculated according to the equations in ref 54.

The initial scaling of the symmetry force constants was carried out on the B3LYP/tz and MP2/tz force constants, employing only frequency data. A very satisfactory fit was achieved using the nine scale factors listed in Table 6. The νCH, νCF, and $\delta_{\parallel}$CH factors were all constrained to be equal in the two in-plane symmetry species. Separate values for each of the νCF and $\delta_{\parallel}$CH factors in these symmetry species were readily obtainable in an 11-parameter refinement, but their differences were within the sum of their standard deviations. The same was not true for the two $\delta_{\parallel}$CF factors. As the data in Table 6 show, both B3LYP and MP2 treatments agree in the size of the difference in this factor, 4−5% in the cis compound and 8−9% in the trans, and on a reversal of its direction between the two compounds. Apart from these $\delta_{\parallel}$CF factors, the differences between a given factor in the two isomers are usually less than 1% and are largely covered by the error, except for the $\delta_{\perp}$CH factor in the MP2 calculations that decreases by 7% from the cis to the trans compound. With this basis, therefore, we have two instances among the MP2 factors and one among the B3LYP factors of serious error in the assumption of identical factors for a particular type of coordinate in two very similar molecules.

Also shown in Table 6 is the quality of the fit, as measured by the sum of the weighted squares of errors, the ranges, average values, and dispersions of the scale factors. For the cis compound, the B3LYP/tz force field is seen to give a significantly better fit than the MP2/tz force field, whereas for the trans, the two calculations are of comparable quality. As expected, the mean scale factor is slightly closer to unity for the DFT approach. It is interesting that low factor values are not confined to the νCH motion, which is the type of motion most strongly influenced by anharmonicity, as discussed above.

Turning to the tz+ calculations, we find that the fit for the trans data is comparable to that with the tz force field, whereas there is a modest reduction in the range and a closer approach to unity in both the B3LYP and MP2 scale factors with the larger basis set. The large values associated with the B_u and B_1 $\delta_{\parallel}$CF factors remain.

With the cis compound, the MP2/tz+ gave an improved fit, and the two $\delta_{\parallel}$CF factors converged on each other. The latter was also found with the B3LYP/tz+ force field. However, the fit with this tz+ force field was significantly poorer in the 1100−1300 cm^{-1} region than that from the tz calculation. This problem was only partly alleviated by lifting the constraints involving the νCF and $\delta_{\parallel}$CH factors in an 11-parameter refinement, which resulted in the A_1 and B_1 factor values drifting apart. A likely explanation for this behavior is error at the B3LYP/tz+ level in the rather large interaction force constants

TABLE 6: Scale Factors for QC Symmetry Force Fields for cis and trans 1,2-Difluoroethylenes

		cis					trans			
		B3LYP(ν)^a		MP2(ν)^a			B3LYP(ν)^a		MP2(ν)^a	
type	*S*	tz	tz+	tz	tz+	*S*	tz	tz+	tz	tz+
νCH	1, 8	0.9327(40)	0.9292(57)	0.8965(75)	0.8967(65)	1, 9	0.9302(41)	0.9270(39)	0.8947(45)	0.8952(39)
νCF	2	1.0014(28)^b	1.0214(40)^b	0.9478(53)^b	0.9705(46)^b	2	0.9942(37)^b	1.0269(35)^b	0.9328(40)^b	0.9680(36)^b
νCF	9	1.0014(28)^b	1.0214(40)^b	0.9478(53)^b	0.9705(46)^b	10	0.9942(37)^b	1.0269(35)^b	0.9328(40)^b	0.9680(36)^b
νCC	3	0.9250(33)	0.9360(48)	0.9255(67)	0.9414(58)	3	0.9280(84)	0.9403(80)	0.9329(97)	0.9495(85)
$\delta_{\|}$CH	4	0.9709(23)^b	0.9803(33)^b	0.9479(45)^b	0.9570(39)^b	4	0.9803(33)^b	0.9771(31)^b	0.9505(37)^b	0.9464(32)^b
$\delta_{\|}$CH	10	0.9709(23)^b	0.9803(33)^b	0.9479(45)^b	0.9570(39)^b	11	0.9803(33)^b	0.9771(32)^b	0.9505(37)^b	0.9464(32)^b
$\delta_{\|}$CF	5	1.0374(26)	1.0030(36)	1.0250(50)	0.9866(42)	5	1.0003(57)	1.0014(53)	0.9971(66)	0.9939(56)
$\delta_{\|}$CF	11	0.9906(29)	0.9949(42)	0.9761(57)	0.9879(50)	12	1.0790(41)	1.0604(38)	1.0755(46)	1.0581(40)
$\delta_{\perp}$CH	6	0.9271(32)	0.9182(46)	0.9443(63)	0.9676(57)	6	0.9186(39)	0.9399(38)	0.8907(42)	0.9232(39)
$\delta_{\perp}$CF	7	0.9651(48)	0.9751(71)	0.9322(86)	0.9632(78)	7	0.9716(35)	1.0003(35)	0.9346(38)	0.9677(35)
w_{skel}	12	0.9302(25)	0.9546(37)	0.8967(48)	0.9322(44)	8	0.9190(68)	0.9149(64)	0.9293(79)	0.9491(70)
range		0.1124	0.0922	0.1285	0.0912		0.1604	0.1455	0.1993	0.1632
average		0.9645	0.9682	0.9436	0.9599		0.9690	0.9764	0.9487	0.9612
σ_n^{c}		0.0373	0.0336	0.0374	0.0272		0.0495	0.0468	0.0535	0.0433
ΣWSE (ν's only)^d		0.84	1.72	3.23	2.46		1.82	1.65	2.33	1.81

[a] Scaled on frequencies only. [b] Constrained equal. [c] Population standard deviation. [d] Sum of weighted squares of errors.

TABLE 7: Comparison of Observed and Calculated (Scaled B3LYPtz+) Centrifugal Distortion Constants (kHz) for cis 1,2-Difluoroethylenes

	d$_0$				^{13}C$_2$	d$_2$	d$_1$
	obsd^a	calcd^b	ϵ(%)^b	ϵ(%)^c	calcd^b	calcd^b	calcd^b
Δ_J	7.2973(60)	6.9806	4.3	3.3	6.6673	5.6391	6.2452
Δ_{JK}	−47.409(69)	−47.5403	0.3	0.4	−45.1044	−30.8855	−37.1352
Δ_K	145.1(36)	149.8788	−3.3	−1.2	142.7950	82.9453	108.5725
δ_J	2.1662(23)	2.0635	4.7	4.2	2.0108	1.7830	1.9092
δ_K	14.02(26)	12.0522	14.0	13.3	11.3765	8.6089	10.4139
		ΣWSE^d	2.089	1.204			

[a] Reference 6; experimental error shown. [b] From the force field scaled on frequencies only. $\epsilon = 100(\mathrm{obsd} - \mathrm{calcd})/\mathrm{obsd}$. [c] After further refinement of $F_{2,2}$, $F_{2,5}$, and $F_{5,5}$ to frequencies Δ_J, Δ_{JK}, Δ_K, and δ_J. [d] Sum of weighted squares of errors in the column above.

TABLE 8: Comparison of Observed and Calculated Centrifugal Distortion Constants (kHz) for trans 1,2-Difluoroethylenes from Force Fields Derived from the Scaled B3LYP/Tz+ Calculation

	d$_0$				^{13}C$_2$			
	obsd^a	calcd	ϵ(%)^{b,c}	ϵ(%)^{b,d}	obsd^a	calcd	ϵ(%)^b	ϵ(%)^{b,d}
Δ_J	0.7684(54)	0.7289	5.1	2.2	0.7456(45)	0.7209	3.3	0.3
Δ_{JK}	−10.640(63)	−10.7851	−1.4	0.9	−10.466(75)	−10.6537	−1.8	0.7
Δ_K	569.07(33)	589.6511	−3.6	0.2	551.77(39)	569.0046	−3.1	0.7
δ_J	0.0327(87)^e	0.0648	−98.2	−101.2	0.0387(30)^e	0.0665	−71.8	−74.4
δ_K	12.2(29)^e	4.2027	65.6	66.3	2.2(19)^e	4.1068	−88.5	−84.9
	ΣWSE		1.658	0.219	ΣWSE		0.959	0.043

	d$_2$				d$_1$			
	obsd^a	calcd	ϵ(%)^b	ϵ(%)^{b,d}	obsd^a	calcd	ϵ(%)^b	ϵ(%)^{b,d}
Δ_J	0.7231(72)	0.6939	4.0	1.3	0.7243(60)	0.7116	1.8	−1.2
Δ_{JK}	−3.205(63)	−3.2081	−0.1	0.4	−4.890(48)	−5.0656	−3.6	−1.8
Δ_K	185.72(39)	191.8511	−3.3	0.0	326.38(81)	334.4424	−2.5	0.8
δ_J	0.0902(39)	0.0850	5.8	4.4	0.0789(16)	0.0749	5.1	3.7
δ_K	1.9(11)^e	4.0437	−114.9	−110.0	5.07(66)^e	4.4770	11.7	13.5
	ΣWSE		2.443	0.860	ΣWSE		1.921	0.741

[a] References 3 and 4, experimental error shown. [b] $\epsilon = 100(\mathrm{obsd} - \mathrm{calcd})/\mathrm{obsd}$. [c] From the force field scaled on ν's only. [d] From the scaled A$_g$ force field further refined to ν's and Δ's (see Table 3S). [e] Datum omitted from the refinement.

$F_{2,3}$, $F_{9,10}$, and $F_{9,11}$, which were not independently scaled. This observation prompts the reflection that differences in scale factors resulting from a close fit to isotopic data may sometimes stem from small errors in the off-diagonal interaction constants rather than from deficiencies in the QC-derived diagonal constants or from differences in the anharmonicities associated with the vibrations involved. Evidence for the presence of the latter in the δCH motions can be seen in Tables 2 and 3 in a slight tendency for δCH frequencies to be predicted higher than observed (negative ϵ_ν) and for δCD frequencies to be predicted slightly lower than observed (positive ϵ_ν).

Centrifugal Distortion Constants. Tables 7 and 8 show the distortion constants calculated with the nine-parameter force fields. Overall, agreement with the experimental values was slightly better for the tz+ basis, and we quote only values for the latter, choosing the B3LYP set. (The MP2 values are very similar). In the case of the cis compound, the calculated values agree with the observed values within 5%, except for δ_K that is too low by 14%.

Now, the cis distortion constants are determined by geometry and the force constants in the A$_1$ class only. Because the diagonal constants are firmly established in the scaling procedure, we tried varying the A_1 off-diagonal constants, one at a time, each along with the corresponding two diagonal constants, to determine if a better fit—one refined to both the frequencies and the distortion constants with all the other force constants constrained to their previous scaled values—could be obtained. No significant improvement in δ_K was achieved in any of these refinements, and this constant was therefore ignored, leaving 5% uncertainties on the other constants. The only force constant found to produce an overall improvement in the fit to the distortion constants was $F_{2,5}$, which changed from 0.170 to 0.084 aJ $Å^{-1}$. The improvement, shown in Table 7, is likely to derive primarily from the concomitant changes in $F_{2,2}$ (6.693 aJ $Å^{-1}$) and $F_{5,5}$ (1.003 aJ)because distortion constants are thought to depend primarily on such diagonal constants. Whereas the change in the value of $F_{2,5}$ is not implausible, the extent of the improvement in the fit and the paucity of the distortion data are such that the physical significance of the change and the question of the differences between ground-state and equilibrium Δ or δ values must be left open. However, Duncan[51] has commented that isotopic *differences* in these distortion constants appear to be independent of the state, so the calculated constants listed in Table 7 for the $^{13}C_2$, d_1, and d_2 isotopomers should be useful in predicting ground-state values for these species from those for the parent isotopomer.

The same dilemma is reached when the more abundant distortion data for the trans rotamer are considered, as in Table 8. Very large differences between observed and calculated values are found for δ_K in the d_0, $^{13}C_2$, and d_2 isotopomers and for δ_J in d_0 and $^{13}C_2$, where the experimental error is, in any case, also very large. However, δ_J is reproduced to within 6% in the d_2 and d_1 species. An exploration of the effect of variations in the off-diagonal A_g force constants showed that the best fit to the remaining data (ignoring also δ_K in d_1) resulted if $F_{2,5}$, $F_{3,4}$, and $F_{3,5}$ together with the diagonal constants $F_{2,2}$, $F_{3,3}$, $F_{4,4}$, and $F_{5,5}$ were separately refined, as shown in Table 3S. The general improvement in the fit, shown in Table 8, leaves the unweighted δ_J and δ_K values no better fitted than before. The changes occurring in the above symmetry force constants for both B3LYP and MP2 refinements are not implausible. The listing of the sum of the weighted squares of errors (ΣWSE) shows that the MP2 force field reproduces the distortion data slightly better than does the B3LYP force field. Also shown in Table 3S are predictions of frequencies or frequency shifts that might help to discriminate between the unrefined (but scaled) force fields and those refined to both frequency and centrifugal distortion data. The values predicted for $\nu_4(d_0)$ and $\nu_3(d_2)$, which were unweighted in the original scaling because of ignorance of their associated gas−liquid frequency shifts, are little affected by the subsequent refinements. However, the $^{13}C_2$ shifts on ν_3 and ν_4 are significantly worse than before, which tends to cast doubt on the physical reality of these changes in the force field that improve the fit to the distortion data.[52] For the present, then, we prefer the force fields scaled to frequency data only.

Discussion of Force Constants. Our preferred symmetry force fields are listed in Table 9 for both cis and trans isomers. They are derived from the two sets of nine scale factors in Table 6. The potential energy distributions (PED) found for these force fields for the d_0 and d_2 species are given in Table 10, and the normal coordinates L^{-1}, in Tables 4S and 5S. Harmonic corrections to the vibrational dependence of the rotational constants and perpendicular amplitudes are found in Tables 6S and 7S.

TABLE 9: Scaled B3LYP/Tz+ Symmetry Force Constants for cis and trans 1,2-Difluoroethylene[a]

cis								
A_1					B_1			
S_1	S_2	S_3	S_4	S_5	S_8	S_9	S_{10}	S_{11}
5.3051					5.2861			
0.1587	6.7788				0.2144	6.2627		
0.0554	0.6186	9.2561						
0.0302	−0.2966	0.1627	0.5422		0.0247	−0.3788	0.5450	
−0.0715	0.1702	0.2771	0.1711	1.0061	−0.1324	0.5532	0.0208	1.3792

trans								
A_g					B_u			
S_1	S_2	S_3	S_4	S_5	S_9	S_{10}	S_{11}	S_{12}
5.2750					5.2768			
0.1857	6.6509				0.1686	6.1666		
0.0594	0.6735	9.2691						
0.0497	−0.3533	0.1415	0.5634		0.0170	−0.3160	0.4909	
−0.1344	0.5739	0.2755	0.0428	1.4232	−0.0758	0.3249	0.1692	1.0570

cis			trans		
A_2		B_2	A_u		B_g
S_6	S_7	S_{12}	S_6	S_7	S_8
0.1405			0.1623		
0.0545	0.2860	0.3041	0.0114	0.3475	0.2110

[a] Units aJ $Å^{-2}$, aJ $Å^{-1}$, or aJ.

TABLE 10: Potential Energy Distributions (PED) (Terms ≥ 10%) for 1,2-Difluoroethylenes[a]

A. cis

	d_0		d_2	
	ν_{calc}	PED	ν_{calc}	PED
A_1	3121.9	$99S_1$	2328.2	$93S_1$
	1714.3	$20S_2$, $77S_3$, $17S_4$	1675.4	$26S_2$, $74S_3$
	1272.4	$18S_2$, $67S_4$	1063.8	$65S_2$, $13S_4$
	1007.5	$66S_2$, $21S_3$, $19S_4$	846.6	$13S_2$, $13S_3$, $79S_4$
	236.4	$104S_5$	234.7	$104S_5$
A_2	832.7	$108S_{10}$	679.5	$94S_{10}$, $39S_{11}$
	502.8	$98S_{11}$	443.7	$14S_{10}$, $69S_{11}$
B_1	3099.8	$100S_6$	2283.6	$100S_6$
	1369.8	$18S_7$, $100S_8$	1211.7	$83S_7$, $39S_8$, $15S_9$
	1132.1	$81S_7$, $21S_9$	940.1	$16S_7$, $66S_8$
	770.0	$10S_7$, $80S_9$	748.3	$80S_9$

B. trans

	d_0		d_2	
	ν_{calc}	PED	ν_{calc}	PED
A_g	3109.2	$99S_1$	2329.0	$92S_1$
	1701.8	$18S_2$, $76S_3$, $24S_4$	1649.5	$24S_2$, $74S_3$, $14S_4$
	1284.4	$14S_3$, $80S_4$	1121.7	$60S_2$, $11S_3$, $10S_4$, $44S_5$
	1140.9	$74S_2$, $39S_5$	935.0	$10S_2$, $77S_4$
	551.5	$17S_2$, $58S_5$	540.7	$15S_2$, $59S_5$
A_u	876.3	$100S_6$	648.1	$98S_6$
	334.1	$99S_7$	324.6	$96S_7$
B_u	3101.9	$100S_9$	2280.2	$100S_9$
	1273.3	$97S_{11}$[b]	1173.0	$99S_{10}$, $11S_{11}$
	1163.7	$97S_{10}$	942.2	$82S_{11}$
	326.4	$13S_{11}$, $109S_{12}$	307.3	$18S_{11}$, $107S_{12}$

[a] B3LYP/tz+ force fields scaled on frequencies only. [b] The contribution of S_{10} to this mode falls from 6.1 to 2.9% on $^{13}C_2$ substitution. This, together with very large differences in the magnitudes and directions of $\partial p/\partial Q_{10}$ and $\partial p/\partial Q_{11}$, which reflect $\partial p/\partial S_{11}$ and $\partial p/\partial S_{10}$, respectively, explains the dramatic fall in the observed intensity of ν_{10} reported in ref 4.

For a comparison of the force constants of the cis and trans compounds with each other and with their respective QC geometries, there is some merit in using the unscaled values if we wish to see an unbiased description of what our QC treatments indicate about all these molecular properties. Unscaled valence force constants from the B3LYP/tz+ calculation

TABLE 11: Unscaled B3LYP/Tz+ Valence Force Constants and Differences for cis and trans 1,2-Difluoroethylenes[a]

type	cis	trans	cis−trans	type	cis	trans	cis−trans
νCH	5.6994	5.6916	0.0078	νCH/νCH	0.0102	−0.0010	0.0112
νCF	6.3838	6.2410	0.1428	νCF/νCF	0.2526	0.2358	0.0168
νCC	9.8895	9.8580	0.0315	νCH/νCC	0.0420	0.0450	−0.0030
$\delta_{\parallel}$CH	0.5545	0.5394	0.0151	νCF/νCC	0.4474	0.4847	−0.0373
$\delta_{\parallel}$CF	1.1947	1.2090	−0.0143	νCH/νCF[b]	0.1915	0.1815	0.0187
τCH	0.1530	0.1727	−0.0197	νCH/νCF[c]	−0.0285	0.0088	−0.0373
τCF	0.2933	0.3474	−0.0541	$\delta_{\parallel}$CH/ $\delta_{\parallel}$CH	−0.0015	0.0371	−0.0386
				$\delta_{\parallel}$CF/$\delta_{\parallel}$CF	−0.1916	0.2122	−0.4038
				τCH/τCF	0.0576	0.0117	0.0459

[a] Units aJ Å^{-2} or aJ. [b] Common carbon atom. [c] Different carbon atoms.

are therefore shown in Table 11. (Scaled values are available in Table 8S.)

The C═C stretching constant ($F_{3,3}$) is predicted to be trivially (0.3%) greater in the cis compound, in agreement with the virtual identity of the computed bond lengths (Table 1). The scaled force constants also agree within 0.2%. The 5% difference in $F_{3,3}$ deduced in the earlier works cited[5,11] is largely due to the failure to correct for resonance and phase shift. However, the C−F stretching constant is perceptibly greater in the cis compound, either scaled or unscaled, and this difference is in keeping with the shorter C−F distance in the cis isomer. The essential identity of the C−H bonds with respect to both length and force constant has been discussed above.

The stretch/stretch interaction constants are similar in the two compounds, except where bonds on opposite carbon atoms are concerned. With the latter, both CH/CH and CH/CF interactions change sign from the cis to the trans isomer such that the interactions between bonds cis to each other are positive, whereas those between bonds trans to each other are negative. This mirrors the pattern found ab initio in ethylene[47] and is reminiscent of the similar differences between gauche- and antiperiplanar-related CH and CF bond-stretching constants in fluoroethanes.[25]

The 2−3° differences in HCC and FCC angles between the two compounds are reflected in small differences in their in-plane bending force constants: as the HCC or FCC angle increases, the bending force constant decreases. For the FCC angle, this change is more noticeable with the scaled valence force constants. Rather larger differences between cis and trans isomers are found in their in-plane bend−bend interactions, which are positive for the trans compound and negative for the cis. The explanation given by Wiberg et al.[10] for the difference in stability of the two compounds, which invokes a greater loss of overlap in the C═C bond of the trans because of rotation of the bonding orbitals, could be extended to explain also why there is a large positive $\delta_{\parallel}$CF/$\delta_{\parallel}$CF bending force constant in the trans. It is not as easy to understand why the same constant should be markedly negative in the cis compound, where steric repulsion between the cis-related fluorines would instead tend to produce a positive value.

Among the out-of-plane bending constants in Table 9, the major effect is the much larger value for this constant in the B_2 species of the cis isomer compared with that for the B_g mode in the trans. This difference has previously been related to the greater stability of the cis compound.[5] By contrast, the constants for the changes in the HCCH and FCCF dihedral angles in the A_2 (cis) and A_u (trans) species are appreciably greater in the case of the trans compound.

TABLE 12: Calculated IR Intensities *A* (km mol^{-1}) for Overlapping Bands in 1,2-Difluoroethylenes

isotopomer	modes	B3LYP/tz *A*	B3LYP/tz+ *A*	MP2/tz *A*	MP2/tz+ *A*	expt[a]
trans d_0	ν_7, A_u	5.5	5.1	5.8	5.2	12.7(14)[b]
	ν_{12}, B_u	13.5	13.8	13.9	14.3	1.5(15)[b]
	ν_7/ν_{12}	0.41	0.37	0.42	0.36	8.5
	$\nu_7 + \nu_{12}$	19.0	18.9	19.7	19.5	14.2
trans d_2	ν_7, A_u	6.6	6.2	6.9	6.3	12.6(15)
	ν_{12}, B_u	11.8	12.1	12.1	12.5	1.4(16)
	ν_7/ν_{12}	0.56	0.51	0.57	0.50	9.0
	$\nu_7 + \nu_{12}$	18.4	18.3	19.0	18.8	14.0
trans d_0/d_2	$\nu_7 + \nu_{12}$	1.033	1.033	1.037	1.037	1.01
trans d_1	ν_7, A′	8.1	8.6	7.0	7.3	
	ν_{10}, A′	39.4	42.2	39.6	43.6	
	ν_7/ν_{10}	0.21	0.20	0.18	0.17	
	$\nu_7 + \nu_{10}$	47.5	50.8	46.6	50.9	44.3(8)
	ν_9, A′	12.5	12.9	12.9	13.3	
	ν_{12}, A″	6.0	5.5	6.3	5.6	
	ν_9/ν_{12}	2.1	2.3	2.0	2.4	
	$\nu_9 + \nu_{12}$	18.5	18.4	19.2	18.9	15.4(2)
cis *d_0*	ν_{11}, B_1	32.8	33.3	31.0	31.3	20.6(3)[c]
	ν_{12}, B_2	42.2	55.4	38.2	51.9	39.0(5)[c]
	ν_{11}/ν_{12}	0.78	0.60	0.81	0.60	0.528
	$\nu_{11} + \nu_{12}$	75.0	88.7	69.2	83.2	59.6
cis d_2	$\nu_{11} + \nu_{12}$[d]	48.3	54.8	44.7	51.3	42.0
cis d_0/d_2	$\nu_{11} + \nu_{12}$	1.55	1.62	1.55	1.62	1.42
cis d_1	ν_8, A′	31.3	31.7	29.6	29.8	
	ν_{10}, A″	15.4	18.5	15.8	20.8	
	ν_8/ν_{10}	2.03	1.71	1.87	1.43	
	$\nu_8 + \nu_{10}$	46.7	50.2	45.4	50.6	37.1(6)

[a] trans—ref 9; cis—ref 8. [b] Graphical separation employed. [c] Separation using the measured d_2 intensities and the G sum rule. [d] These bands do not overlap each other.

TABLE 13: Directions α (deg) of $\partial p/\partial Q$ in the In-Plane B_u Vibrations of *trans*-1,2-$C_2H_2F_2$[a]

mode	B3LYP/tz	B3LYP/tz+	MP2/tz	MP2/tz+
Q_9	63.0	47.3	57.1	42.6
Q_{10}	30.3	26.7	32.3	29.7
Q_{11}	−137.2	−136.4	−136.0	−135.1
Q_{12}	129.8	131.8	131.6	133.8

[a] α is measured clockwise from the C(1) → C(2) direction, as in Figure 1A. Figure 1A also defines the phase of each *Q*.

Interpretation of Spectra: Infrared Intensities and Dipole Derivatives.

Overlapping Bands. The reassignments of ν_7 and ν_{12} (d_0, d_2) and of ν_9 and ν_{12} (d_1) in the trans isomer prompt a reexamination of the way the experimental intensity has been divided in each of these pairs of overlapping bands. Even without this reassignment, the calculated intensities, listed in Table 12, give a very different ratio for the intensities of the upper and lower bands than that previously obtained by a graphical separation. Whereas these calculated intensities strictly apply only to the unscaled frequencies, the changes due to differences between the unscaled and scaled normal coordinates are expected to be small.

The results for trans d_0 and trans d_2 are very similar. The ratio of A_7/A_{12} is somewhat basis set-dependent but clearly makes the ν_7 band about 40% as intense as the ν_{12} band. The sum $A_7 + A_{12}$ falls only slightly from d_0 to d_2, and for this sum, there is good agreement on the relative fall between calculated and observed data. The only route to a reliable experimental value of the ratio A_7/A_{12} would be a careful simulation of a high-resolution infrared spectrum of this pair of Coriolis-interacting bands. For a first approximation of such an analysis, see the end of the "Region below 600 cm^{-1}(trans)" section. There, the significant difference in intensities of the Q-branch lines on the two sides of the distorted band is described.

Experimental separation of the intensity in the two overlapping pairs of bands in the *trans*-d_1 species has not been attempted, but the calculated ratios and sums are included in Table 12 for future use.

TABLE 14: Atomic Polar Tensors for 1,2-$C_2H_2F_2$[a]

A. cis

	C(1)			H(4)			F(3)		
	∂x	∂y	∂z	∂x	∂y	∂z	∂x	∂y	∂z
∂p_x	0.5926	−0.6371	0.0000	−0.0051	−0.0018	0.0000	−1.1397	0.0202	0.0000
∂p_y	−0.4283	0.7481	0.0000	−0.0492	0.0405	0.0000	−0.3377	−0.2364	0.0000
∂p_z	0.0000	0.0000	−0.0918	0.0000	0.0000	0.1834	0.0000	0.0000	−0.0915

B. trans

	C(1)			H(4)			F(3)		
	∂x	∂y	∂z	∂x	∂y	∂z	∂x	∂y	∂z
∂p_x	0.5456	−0.6628	0.0000	0.0051	−0.0013	0.0000	−1.1370	0.0326	0.0000
∂p_y	−0.2489	0.7898	0.0000	−0.0488	0.0376	0.0000	−0.3339	−0.2411	0.0000
∂p_z	0.0000	0.0000	−0.0776	0.0000	0.0000	0.2104	0.0000	0.0000	−0.1328

[a] B3LYP/tz+ calculations; axes as in Figure 1B and values given in units of *e*.

TABLE 15: Dipole Derivatives with Respect to Stretching of the C−H and C−F Bonds

	B3LYP/tz		B3LYP/tz+		MP2/tz		MP2/tz+	
	cis	trans	cis	trans	cis	trans	cis	trans
				C−H Bond				
$\partial p_x/\partial x^a$	−0.027	−0.016	−0.005	0.005	−0.020	−0.007	0.000	0.013
$\partial p_y/\partial x^a$	−0.041	−0.039	−0.049	−0.049	−0.044	−0.039	−0.052	−0.048
$\lvert\partial\mu/\partial r\rvert^b$	0.049	0.042	0.049	0.049	0.049	0.040	0.052	0.049
θ^c	123.1	112.8	95.9	84.0	114.1	100.1	90.5	75.0
$q_H{}^d$	0.115	0.122	0.151	0.164	0.112	0.121	0.156	0.170
				C−F Bond				
$\partial p_x/\partial x^a$	−1.087	−1.071	−1.140	−1.137	−1.054	−1.036	−1.107	−1.101
$\partial p_y/\partial x^a$	−0.338	−0.330	−0.338	−0.334	−0.317	−0.306	−0.315	−0.306
$\lvert\partial\mu/\partial r\rvert^b$	1.138	1.121	1.189	1.185	1.101	1.081	1.151	1.143
θ^c	162.7	162.9	163.5	163.6	163.3	163.6	164.1	164.5
$q_F{}^d$	−0.206	−0.214	−0.134	−0.138	−0.217	−0.225	−0.129	−0.128

[a] Components of the APT (*e*) when the *x* axis lies along the bond concerned. *y* axes oriented as in Figure 1B. [b] Dipole derivative with respect to stretching of the CH or CF bond (*e*). [c] Angle (deg) between $\partial\mu/\partial r$ and the CH or CF bond, as defined in Figure 1B. [d] Mulliken charge (*e*).

In the cis compound, there is less need for a similar treatment of the overlapping pair of bands ν_{11} and ν_{12} in the d_0 species because these two bands are well-separated in the d_2 isotopomer.[8] The ratio A_{11}/A_{12} in cis d_0 can then be estimated from the cis d_2 intensities using the G sum rule.[8] The agreement shown in Table 12 between this value and those from the tz+ calculations is quite good, probably within the likely error in both approaches. The ratio $(A_{11} + A_{12})(d_0)/(A_{11} + A_{12})(d_2)$ is somewhat smaller from experiment than from the tz+ calculations. We note that the QC calculations here will involve additional error due to overestimation of the permanent dipole moment μ_{mol} of the molecule because rotational corrections are involved with all the infrared-active bands in the cis isomer. This may explain the better agreement with the tz basis that yields the smaller μ_{mol}.

Data are given also in Table 12 for the mildly overlapping pair ν_8 and ν_{10} in cis d_1.

Direction of $\partial \boldsymbol{p}/\partial Q$. As discussed above, QC calculations of the direction of $\partial \boldsymbol{p}/\partial Q$ are needed for the evaluation of atomic polar tensors from experimental intensities, where this direction is not dictated by symmetry. Table 13 lists the angle α that we calculate for each of the B_u modes of *trans*-1,2-$C_2H_2F_2$. The definition of this angle α and the phase of each normal coordinate *Q* are shown in Figure 1A. We are unable to reproduce any of the angles reported in ref 15 for MP2 calculations with the same basis sets on either choice of phase for *Q*.[53] In particular, the directions we obtain for $\partial \boldsymbol{p}/\partial Q_9$, the CH stretching mode, though sensitive to the basis set, are quite different from those in Figure 2 of ref 15, though fairly similar to those shown there for the same mode in the chloro compound. (For the latter, we obtain from the B3LYP/tz+ calculation a value of −24° compared with −47° for the fluoride.) The fluoro value receives confirmation from experiment in that in the more recent spectra the band due to ν_9 in both the d_0 and $^{13}C_2$ isotopomers is plainly type A in contour.

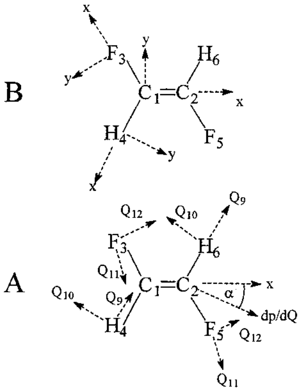

Figure 1. (A) Definition of the angle α giving the direction of $\partial p/\partial Q_i$ for the in-plane modes of *trans*-1,2-$C_2H_2F_2$ and the phase of each normal coordinate Q_i of the B_u symmetry species. Amplitudes are not to scale. (B) Definitions of the *x, y* axis systems for the atomic polar tensors of Table 14.

Related to this change in direction of $\partial \boldsymbol{p}/\partial Q_9$ is a very different direction for $\partial \boldsymbol{\mu}/\partial r$ for the CH bond. The components of $\partial \boldsymbol{\mu}/\partial r_{CH}$ constitute the *x* column of the atomic polar tensor (APT) when the latter is referred to an axis system in which the *x* axis lies along the CH bond. APTs from the B3LYP/tz+ calculation are given in Table 14. Magnitudes and directions of $\partial \boldsymbol{\mu}/\partial r$ are shown in Table 15 for both CH and CF bonds, together with the corresponding Mulliken charges on the H and F atoms.

Whereas the direction of $\partial\boldsymbol{\mu}/\partial r_{CH}$ is quite sensitive to the basis and level of calculation, differing also significantly from cis to trans, in all cases, it is not far from being perpendicular to the CH bond. There is no obvious connection between $\partial\boldsymbol{\mu}/\partial r_{CH}$ and the Mulliken charge q, which is not surprising in a parameter dominated by flux terms.[13] By contrast, $\partial\boldsymbol{\mu}/\partial r_{CF}$ is remarkably stable in its direction, which is close to that of the CF bond.

The data in Table 15, together with the $\partial\boldsymbol{p}/\partial y$ data of Table 14, allow us to reexamine the question as to how far the in-plane elements of the APTs are transferable, as has been claimed,[9,12,15] from the cis to the trans isomer. The similarity is certainly very strong. Differences in $\partial\boldsymbol{\mu}/\partial r$ that might have been anticipated from differences in the Mulliken charge q are absent. A few small but consistent differences are found, notably in $\partial p_x/\partial x$, which determines the direction of $\partial\boldsymbol{\mu}/\partial r_{CH}$, and also in $\partial p_x/\partial y$. However, these small differences are unlikely to be detectable in improved experimental values of the APTs, bearing in mind the various sources of error that will inevitably remain there.

It is very clear from the data in Table 14 that the transferability of the APTs does not extend to the out-of-plane elements p_{zz}, which are equal to the equilibrium or static charges on each atom.[13] There are real differences in these charges on the hydrogen and fluorine atoms, which yield directly the corresponding CH and CF bond moments between the cis and trans compounds, as has been previously observed.[9,12,13,15] (The experimental values of these differences for the H atom and the C−H bond will be little affected by the change in the allocation of intensity between the ν_7 and ν_{12} necessitated by the present study because of the low intensity associated with both of these modes.)

The present results indicate a pressing need for redeterminations of the experimental APTs of the cis and trans compounds, which would depend on high-resolution methods. For both species, superior normal coordinates are now available, whereas for the trans, there are redistributions of intensity as well as new directions for $\partial\boldsymbol{p}/\partial Q$ to be taken into account.

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Supporting Information Available: Infrared and Raman frequencies and assignments for 1,2-$C_2H_2F_2$-$^{13}C_2$ (cis, Table 1S; trans, Table 2S); trans A_g force field refined to centrifugal distortion and frequency data (Table 3S); normal coordinate matrices L^{-1} for cis (Table 4S) and trans (Table 5S); harmonic corrections to rotational constants and perpendicular amplitudes for cis (Table 6S) and trans (Table 7S); scaled valence force constants for both isomers (Table 8S). This material is available free of charge via the Internet at http://pubs.acs.org.

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