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A Comparison of Predicted and Experimental Vibrational Spectra in Some Small Fluorocarbons

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Abstract: The vibrational assignments of difluoromethane, *cis* and *trans* 1,2-difluoroethylene, trifluoroethylene, 2-fluoropropene, 1,1-difluoroethylene, and tetrafluoroethylene have been reassessed in the light of recent theoretical work. Inconsistent experimental wave number values and assignments have been clarified, and some changes to the experimental assignments are proposed. The assignments compare favorably with recent scaled density functional theory calculations using the hybrid three-parameter B3-PW91 density functional.

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Key words: fluorocarbons; scaled quantum mechanical predictions; infrared spectrum; Raman spectrum; scaled density functional theory

Introduction

Small fluorocarbons are being extensively studied as potential atmospheric pollutants due to their increased use in industry as replacements for ozone-depleting CFC and HCFC species. The vibrational spectra of these species are of interest both for trace gas detection and quantification, and for predicting thermodynamic behavior. These molecules have been the subject of many studies over a number of years, but the experimental identification of vibrational fundamentals is often uncertain due to overlap of the rotational envelopes of the numerous bands and the presence of interfering hot bands. We and others have recently developed experimental techniques based around jet-cooled FTIR spectroscopy[1,2] and collisional and enclosive flow cooling[3,4] aimed primarily at high-resolution spectroscopy. These techniques also significantly reduce the rotational envelopes and hot band clutter in low-resolution spectra as well, allowing more accurate and certain assignments of spectra. Theory can also provide significant aid in eliminating band assignment uncertainties, and we have used simple scaled quantum mechanical calculations to assist assignments.[5] Recently Baker and Pulay[6] derived a set of optimal scaling factors applicable directly to the individual primitive force constants obtained from both HF/6-31G(d) and density functional theory calculations using the hybrid three-parameter B3-PW91 density functional. This was achieved by a least-squares fit to the experimentally observed fundamentals of 12 "simple" fluorocarbons. The scaling factors from the training set were then used to predict the vibrational spectra of all possible fluoromethanes, fluoroethylenes, fluoroethanes, and monofluoropropenes using the Scaled Quantum Mechanical (SQM) force field procedure. The agreements between predicted and the experimental vibrational wave number values for species with complete and certain assignments was good, particularly for the DFT. Here, we set out to reexamine the vibrational spectra of those species where experimental data was incomplete, lacking or unreliable. In some cases a reassessment of the literature was adequate to arrive at reliable assignments, whereas in others new spectral data has been collected to confirm assignments or arrive at consistent assignments. In this article, we make further comparison of the SQM-DFT predictions and experimental fundamentals for seven simple fluorocarbons, and obtain general agreement similar to that found by Baker and Pulay.

Experimental

Infrared spectra were recorded on a Bruker HR120 high-resolution FTIR spectrometer using a White cell at room temperature and set at 20-m path length or supercooled in our enclosive flow cell.[4] The spectrometer was equipped in the far-IR with a mylar beamsplitter and DTGS detector and in the mid-IR with a KBr based beamsplitter and composite MCT/InSb detector. Raman spectra were recorded on a Renishaw micro-Raman 2000 system with a HeNe laser (632 nm) using a macro-objective. Samples were cooled in a sealed pyrex tube for the Raman experiments.

Table 1. Predicted and Experimental Fundamentals (cm^{-1}) for Difluoromethane.

Symmetry		Experimental	SQM/B3-PW91	
		IR	Calc.	IR int./km mol^{-1}
A_1	ν_4	528.5[a]	533	1.5
B_2	ν_9	1090.1[b]	1107	210
A_1	ν_3	1111.6[b]	1112	100
B_1	ν_7	1178.6[c]	1162	19
A_2	ν_5	1255.8[c]	1245	—
B_2	ν_8	1435.6[d]	1457	46
A_1	ν_2	1509.2[d]	1504	4.4
A_1	ν_1	2948[a]	2934	54
B_1	ν_6	3014.1[e]	2997	73

rms deviation: 13.6 cm^{-1}
average deviation: 11.9 cm^{-1}
max deviation: ~21 cm^{-1}

[a] ref. 11.
[b] ref. 15.
[c] ref. 13.
[d] ref. 12.
[e] ref. 14.

Results and Discussion

Difluoromethane

Difluoromethane is an asymmetric top with C_{2v} symmetry, and has nine fundamentals classified as $4A_1 + 2B_1 + 2B_2 + A_2$. The initial vibrational assignments proposed by Stewart and Nielsen[7] were revised somewhat by Rank et al.[8] Plyler and Benedict,[9] and Holzer.[10] The assignments of the later three investigators were essentially confirmed, and more accurate band centres derived by Suzuki and Shimanouchi.[11] The latter are internally consistent and consistent with the recent SQM calculations of Baker and Pulay.[6] Some bands have been recently studied by high-resolution IR techniques,[12–15] and the results are consistent with the earlier studies and give precise band origins. The experimental wave number values, taken from Suzuki and Shimanouchi[11] and the high-resolution IR studies[12–15] and their assignments, together with the predicted fundamentals, are shown in Table 1. The agreement between experimental and SQM is very good with rms, average, and maximum deviations between theory and experiment for all nine fundamentals of 13.6 cm^{-1}, 11.9 cm^{-1}, and ~21 cm^{-1}.

1,2-Difluoroethylene

1,2-Difluoroethylene has separate *cis* and *trans* conformers. The *cis* conformer has C_{2v} symmetry, and its 12 fundamentals are distributed in $5A_1$, $2A_2$, $4B_1$, and B_2. The *trans* conformer has C_{2h} symmetry, and its 12 fundamentals are distributed in $5A_g$, $2A_u$, B_g, and $4B_u$. After some preliminary assignments by early workers, Craig and coworkers[16,17] obtained a complete and consistent wave number assignment for the two isomers using liquid-phase Raman spectra, and infrared spectra in the gas phase and cold matrix. High-resolution IR studies of both the *trans* conformer[18] and the *cis* conformer[19–21] provided some more precise band origins. Tables 2 and 3 show the experimental fundamentals and assignments—mostly taken from the gas-phase IR and liquid-phase Raman study of Craig and Overend along with the SQM theoretical prediction.[6]

The *cis* conformer assignment is in good agreement with SQM predictions for all wave number values except for some discrepancies with the C—H stretch region. C—H fundamentals are often difficult to assign accurately due to overlapping bands and Fermi resonance. *cis* 1,2-Difluoroethylene is a case in point. The assignments of these fundamentals are inconsistent in the literature, with the Craig assignment[17] the most recent. With assignment of the 3135 cm^{-1} band to ν_8 the difference from the SQM predictions is 40 cm^{-1}, which is larger than all the deviations from all other molecules studied and even worse, the energy ordering of ν_1 and ν_8 are reversed. A low-resolution, room-temperature spectrum recorded in the laboratory of Giorgianni[22] reveals a blended contour that appears to confirm the Craig assignments. A solution to this dilemma, hinted at by McKean[23] is found in the position of the strong $\nu_2 + \nu_9$ (B_1) combination band at 3151 cm^{-1}, shifted ca. 40 cm^{-1} by Fermi resonance with ν_8. This implies that the unperturbed ν_8 vibration is found at ca. 3095 cm^{-1}, now in excellent agreement with the SQM value. After reassignment is made, the rms, average, and maximum deviation between theory and experiment for 12 fundamentals are 9.3 cm^{-1}, 7.2 cm^{-1}, and 19 cm^{-1}.

For the *trans* conformer, the agreement between the experiment and theory is generally in good agreement as shown in Table 3.

Table 2. Predicted and Experimental[17] Fundamentals (cm^{-1}) for *cis* 1,2-Difluoroethylene.

Symmetry		Experimental		SQM/B3-PW91	
		IR	Raman	Calc.	IR int./km mol^{-1}
A_1	ν_5	237 m	241 w	229	2.1
A_2	ν_7	—	495 s	494	—
B_2	ν_{12}	756 s	—	775	34
B_1	ν_{11}	769 s	—	780	33
A_2	ν_6	—	839 m	837	—
A_1	ν_4	1016.0 s[a]	1004 s	1008	58
B_1	ν_{10}	1131.2 s[b]	1109 vw	1137	104
A_1	ν_3	1263 s	1251 m	1262	34
B_1	ν_9	1374 s	1360 vw	1383	37
A_1	ν_2	1718.8 s[c]	1712 vs	1736	47
B_1	ν_8	3095 m[d]	—	3095	0.3
A_1	ν_1	3122 m	3130 vs	3118	13

rms deviation: 9.3 cm^{-1}
average deviation: 7.2 cm^{-1}
max deviation: 19 cm^{-1}

[a] ref. 20.
[b] ref. 19.
[c] ref. 21.
[d] corrected for Fermi resonance shift, see text. The uncorrected band position is 3135 cm^{-1}.

Table 3. Predicted and Experimental[17] Fundamentals (cm^{-1}) for *trans* 1,2-Difluoroethylene.

Symmetry		Experimental		SQM/B3-PW91	
		IR	Raman	Calc.	IR int./km mol^{-1}
B$_u$	ν_{12}	341 m	338 m	319	11
A$_u$	ν_7	324 m	—	334	5.0
A$_g$	ν_5	—	548 s	556	—
B$_g$	ν_8	—	788 s	791	—
A$_u$	ν_6	874 s	—	902	59
A$_g$	ν_4	—	1123 m	1154	—
B$_u$	ν_{11}	1159 vs	—	1166	262
A$_g$	ν_3	—	1286	1278	—
B$_u$	ν_{10}	1274 m	—	1279	35
A$_g$	ν_2	—	1694 vs	1721	—
B$_u$	ν_9	3114 m	—	3103	15
A$_g$	ν_1	—	3111 vs	3111	—

rms deviation: 16.8 cm^{-1}
average deviation: 13.3 cm^{-1}
max deviation: 31 cm^{-1}

The rms, average, and maximum deviation between theory and experiment for 12 fundamentals are 16.8 cm^{-1}, 13.3 cm^{-1}, and 31 cm^{-1}. The larger deviations here are due to a number of the wave number values being accessible only from the liquid Raman data. The predictions are for gas phase molecules, and the shifts due to the liquid state of the sample cannot be taken into account.

Trifluoroethylene

Experimental data comes from a very early gas-phase low-resolution infrared study[24] and high-resolution infrared studies.[25–27] Because trifluoroethylene has C$_s$ symmetry all 12 fundamentals (9A$'$ + 3A$''$) are infrared active. The experimental wave number values and their assignments, together with the SQM predicted fundamentals, are shown in Table 4. The agreement in wave number position is again very good. The rms, average, and maximum deviation between theory and experiment for 12 fundamentals are 7.8 cm^{-1}, 6.5 cm^{-1}, and 15 cm^{-1}. It should be noted that the ν_1 fundamental has been corrected for Fermi resonance by Mann et al.[24] leading to excellent agreement even for the C—H mode.

2-Fluoropropene

The 2-fluoropropene molecule belongs to C$_s$ symmetry and its 21 fundamental vibrations are distributed in 14A$'$ and 7A$''$, and all vibrations are infrared and Raman active.

The basic experimental data comes from an early gas-phase IR and solid-phase Raman study by Crowder and Smyrl[28] and a study of the internal rotation barrier by Bell et al.[29] The experimental wave number values, some reassigned by us as described below, together with the SQM predictions[6] are shown in Table 5. The original assignment of Crowder and Smyrl[28] in the high wave number region is generally compatible with the SQM predictions;

however, there are a few exceptions. The assignment of the low wave number modes is in error in that the assignments of ν_{14}, ν_{13}, and ν_{19} at 352 cm^{-1}, 404 cm^{-1}, and 629 cm^{-1}, respectively, deviate by 47, 75, and 107 cm^{-1}, which is well outside the expected error, especially for low wave number modes. Furthermore, SQM predicts that two fundamentals, one A$'$ and other one A$''$, occur very close together around 476 cm^{-1}. A reassessment of the spectrum in the light of the above leads to the assignment in Table 5. The very weak ν_{19} band is not observed and the 404 cm^{-1} band is assigned to ν_{14}. The ν_{20} band lies essentially on top of the more intense ν_{13} band at 472 cm^{-1}. Some reassignment appears warranted in the vicinity of 1400 cm^{-1} also. The ν_7 and ν_8 bands, predicted to be at 1400 cm^{-1} and 1375 cm^{-1}, respectively, were originally assigned to features at 1429 and 1401 cm^{-1}.[28] The strong IR band observed at 1401 cm^{-1}, however, matches the calculated value for ν_7 much better. Also, the solid-phase Raman spectrum has a previously unassigned, medium strength band at 1374 cm^{-1} and the IR spectrum shows that the 1401 cm^{-1} band has a shoulder feature around 1375 cm^{-1}, which we assign to ν_8. After these reassignments are made, the rms, average, and maximum deviation between theory and experiment for 20 fundamentals observed are 9.7 cm^{-1}, 7.5 cm^{-1}, and 15 cm^{-1}. The sheer number of vibrations means that some of the bands are overlapped, leading to a few uncertain assignments, for example, around 1450 cm^{-1}. Spectra of cooled sample are needed to make further progress, although the SQM predictions are of considerable help.

1,1-Difluoroethylene

1,1-Difluoroethylene is planar with C$_{2v}$ symmetry and has 12 vibrational modes distributed in 5A$_1$, 1A$_2$, 4B$_1$, and 2B$_2$. Most of

Table 4. Predicted and Experimental[24] Fundamentals (cm^{-1}) for Trifluoroethylene.

Symmetry		Experimental	SQM/B3-PW91	
		IR	Calc.	IR int./km mol^{-1}
A$'$	ν_9	232 w	231	3.9
A$''$	ν_{12}	305 w	301	4.0
A$'$	ν_8	485 w	493	1.2
A$''$	ν_{11}	555 vw	558	1.0
A$'$	ν_7	623 m	629	2.3
A$''$	ν_{10}	750 s	762	31
A$'$	ν_6	929 s	927	59
A$'$	ν_5	1172.7^a vs	1167	134
A$'$	ν_4	1264.9^b vs	1267	179
A$'$	ν_3	1361.4^c vs	1371	120
A$'$	ν_2	1788 s	1798	70
A$'$	ν_1	3150 m	3135	6.8

rms deviation: 7.8 cm^{-1}
average deviation: 6.5 cm^{-1}
max deviation: 15 cm^{-1}

^{a}ref. 25.
^{b}ref. 26.
^{c}ref. 27.

Table 5. Predicted and Experimental[28] Fundamentals (cm^{-1}) for 2-Fluoropropene.

Symmetry		Experimental		SQM/B3-PW91	
		IR	Raman (solid)	Calc.	IR int/km mol^{-1}
A″	ν_{21}	191	—	198	0.5
A′	ν_{14}[a]	404 w	400	399	0.5
A″	ν_{20}	472 m	478	473	1.6
A′	ν_{13}[a]	472 m	478	479	5.4
A″	ν_{19}[a]	—	—	736	0.1
A′	ν_{12}[a]	846 s	862	838	15
A″	ν_{18}	846 s	837	840	69
A′	ν_{11}	944 m	939	942	29
A′	ν_{10}	1008 w	1008	1010	6.5
A″	ν_{17}	1048 m	1050	1055	2.8
A′	ν_{9}	1270 s	—	1285	82
A′	ν_{8}[a]	1375 sh	1374	1375	14
A′	ν_{7}[a]	1401 m	1397	1400	18
A″	ν_{16}	1448 m	1444	1441	8.1
A′	ν_{6}	1458 m	1444	1456	8.9
A′	ν_{5}	1687 s	1689	1710	97
A′	ν_{4}	2942 m	2927	2922	14
A″	ν_{15}	2975 m	2964	2981	12
A′	ν_{3}	3012 m	3026	3027	11
A′	ν_{2}	—	3059	3064	0
A′	ν_{1}	3141 w	3135	3151	3.9

rms deviation: 9.7 cm^{-1}
average deviation: 7.5 cm^{-1}
max deviation: 15 cm^{-1}

[a]Reassigned transition wave number values.

the fundamentals have been studied[29–37] with high-resolution spectroscopy and the band centers are as shown in Table 6. The agreements in position between experiment and theory are good. However, the assignments from previous low resolution studies[38–40] for the weak fundamentals that lacked high-resolution analysis contain some inconsistencies that, for the C—H modes, have been addressed by McKean.[23] To clarify some of the other problems, we have recorded liquid-phase Raman spectra and both room-temperature and low-temperature gas-phase infrared spectra for this molecule.

There is considerable disagreement over the position of the IR forbidden (A$_2$ symmetry) ν_6, torsional mode. Smith et al.[38] and McKean[23] observed very weak peaks at 590 and 592 cm^{-1} in the gas-phase Raman and IR spectrum, respectively, and assigned them to ν_6, while Oskam and Elst[39] found a weak peak at 561 cm^{-1} under the same experimental conditions and attributed it to ν_6. Edgell and Byrd[40] reported an absence of peaks in these two regions in the liquid-phase Raman spectrum, but instead observed a very weak peak at 714 cm^{-1} and assigned it to ν_6, which is in good agreement with the SQM theoretical predictions. We did not observe this peak in our liquid-phase Raman spectrum despite obtaining high S/N spectrum through co-addition. There is indirect supporting evidence for such an assignment, however, from high-resolution FTIR measurements. Visinoni et al.[34] assigned ro-vibrational transitions of a b-type band at 1320 cm^{-1}. They considered this band to be the $3\nu_{10}$ overtone, which has the required B$_1$

symmetry. However, the ν_{10} fundamental and first overtone occur at 437 cm^{-1} and ~869 cm^{-1}, and therefore $3\nu_{10}$ would be expected at around 1300 cm^{-1}. In addition, the linear deviation in rotational constants shown with vibrational quantum number $\nu_{10} = 0,1,2$ states is in sharp contrast to the constants of the 1320 cm^{-1} band. The only feasible alternative assignment of the 1320 cm^{-1} band is to the $\nu_6 + \nu_{12}$ combination that has required B$_1$ symmetry, implying that ν_6 lies around 709 cm^{-1}, ignoring the $\nu_8/\nu_6 + \nu_{12}$ Fermi resonance shifts.

Additionally, there was inconsistency in the assignment of the ν_3 band with 1363, 1414, and 1405 quoted for the gas phase in previous studies.[38,39] We observed a weak peak at 1365 cm^{-1} in the enclosive flow cooling infrared spectrum, which was a weak and indistinct shoulder on the much more intense ν_8 band at room temperature. In the cold spectrum this band is compatible with an a- or b-type band, and we assign it as ν_3. Our study supports Oskam's[39] assignment, which is in good agreement with the theoretical prediction. Finally, previous studies[38,39] observed a peak around 3110 cm^{-1} and assigned it as B$_1$ mode ν_7, which is 77 cm^{-1} from the SQM prediction and a strong band rather than a weak IR band as predicted. We observe this peak in both our Raman and infrared spectra, but assign it as a combination of ν_2 and ν_3 (symmetry A$_1$), which is shifted up by around 20 cm^{-1} due to Fermi resonance with ν_1. Because we observed a very weak peak in the region 3160–3175 cm^{-1} in the low-temperature infrared and at 3170 cm^{-1} in the Raman spectra, we assign it to the B$_1$

Table 6. Predicted and Experimental Fundamentals (cm^{-1}) for 1,1-Difluoroethylene.

Symmetry		Experimental			SQM/B3-PW91	
		Raman (liq)[a]	IR (gas)[a]	IR (high res)[b]	Calc.	IR int/km mol^{-1}
B_1	ν_{10}	430 w	—	436.9	443	0.6
A_1	ν_5	544 w	551 w	549.9	562	3.0
B_2	ν_{12}	601 m	611 vw	—	621	1.9
A_2	ν_6	714 vw[c]	709[d]		704	—
B_2	ν_{11}	806 w	804 m	802.1	791	89
A_1	ν_4	916 vs	924 s	925.8	923	66
B_1	ν_9	949 vw	954 m	953.8	946	16
B_1	ν_8	—	1303 vs	1301.3	1331	223
A_1	ν_3	1354 m	1365 vw	—	1375	2.3
A_1	ν_2	1730 vs	1727 vs	1728.5	1747	277
A_1	ν_1	3053 m	3080[e] m	3058.1	3092	5.1
B_1	ν_7	3170 w	3174[e] vw	—	3187	0.0

rms deviation: 13.3 cm^{-1}
average deviation: 11.5 cm^{-1}
max deviation: 30 cm^{-1}

[a]This work.
[b]From refs. 29–37 (values truncated).
[c]Ref. 40.
[d]See discussion in text.
[e]From ref. 23, where ν_1 is corrected to take account of the Fermi resonance shift.

mode ν_7, which fits nicely to SQM prediction in both position and relative intensity, and is in agreement with McKean.[23] After these reassignments are made, the rms, average, and maximum deviation between theory and experiment for 12 fundamentals are 13.3 cm^{-1}, 11.5 cm^{-1}, and 30 cm^{-1}. Perhaps not surprisingly, the largest deviation is found for the ν_8 vibration, which is affected by a Fermi resonance.

Tetrafluoroethylene

Tetrafluoroethylene has D$_{2h}$ symmetry and its 12 vibrational modes, distributed as 3A$_g$, 2B$_{1g}$, B$_{2g}$, A$_u$, B$_{1u}$, 2B$_{2u}$, and 2B$_{3u}$ are either IR or Raman active. Assignments based on gas phase IR and gas and liquid phase Raman spectra were summarized by Shimanouchi.[41] These are given in Table 7, together with the SQM predictions. The agreement is excellent, with the rms, average, and maximum deviation between theory and experiment being 8.5 cm^{-1}, 7.1 cm^{-1}, and 18 cm^{-1}.

Discussion and Conclusions

The crucial test of a set of scaling factors obtained by the SQM procedure is their transferability, i.e., how well do they predict a vibrational spectrum, *a priori*. The compilation of experimental data comprising 89 vibrational modes from 7 new molecules provides an excellent test for the B3-PW91/6-31G(d) scaling factors derived by Baker and Pulay,[6] and the results are more than satisfactory. Overall, the rms deviation is 11.5 cm^{-1}, the average error is 9.0 cm^{-1}, and the maximum deviation is 31 cm^{-1}. The

average error is very similar indeed to the 10 cm^{-1} that Baker and Pulay suggest can be expected.

There is just one conspicuous problem—the double bonded carbon–carbon stretch modes are consistently overpredicted. SQM predictions of this mode have now been compared with experiment for a total of eight molecules, including six molecules in our data

Table 7. Predicted and Experimental[41] Fundamentals (cm^{-1}) for Tetrafluoroethylene.

Symmetry		Experimental		SQM/B3-PW91	
		IR	Raman	Calc.	IR int/km mol^{-1}
A_u	ν_4	[190]	—	192	—
B_{2u}	ν_{10}	218 s	—	207	4.5
A_g	ν_3	—	394 w	403	—
B_{1u}	ν_7	406 s	—	415	3.8
B_{2g}	ν_8	—	508 s (liq)	498	—
B_{1g}	ν_6	—	551 m (liq)	559	—
B_{3u}	ν_{12}	558 s	—	561	0.6
A_g	ν_2	—	777.9 s	779	—
B_{3u}	ν_{11}	1186 vs	—	1182	360
B_{2u}	ν_9	1337 vs	—	1329	384
B_{1g}	ν_5	—	1340 vw	1358	—
A_g	ν_1	—	1872 m	1874	—

rms deviation: 8.5 cm^{-1}
average deviation: 7.1 cm^{-1}
max deviation: 18 cm^{-1}

set and the two conformers of 3-fluoropropene listed by Baker and Pulay.[6] The average deviation is -19.5 cm^{-1}. In the SQM treatment, a common scaling factor was applied to both single and double carbon–carbon bonds. Possibly they require separate scaling factors. Alternatively, the problem may simply be that the training set was somewhat deficient in this regard as only two molecules with a C=C double bond were included—fluoroethylene and 3,3,3-trifluoro-2-methylpropene.

The overall quality of the SQM predictions was such that previous vibrational assignments were able to be critically assessed. On this basis, we have proposed reassignments of some of the fundamentals in 2-fluoropropene, and a reanalysis of the C—H stretching mode in *cis* 1,2-difluoroethylene. We have also clarified the experimental assignments for the fundamentals of 1,1-difluoroethylene in the literature.

Acknowledgments

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