

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243980721>

Conformational stability, r o structural parameters, barriers to internal rotation, ab initio calculations, and vibrational assignment for 2,2-difluoroethanol

ARTICLE *in* STRUCTURAL CHEMISTRY · JUNE 2009

Impact Factor: 1.84 · DOI: 10.1007/s11224-009-9446-8

CITATIONS

4

READS

35

6 AUTHORS, INCLUDING:



Arindam Ganguly

University of Missouri - Kansas City

35 PUBLICATIONS 187 CITATIONS

SEE PROFILE



Gamil A. Guirgis

College of Charleston

341 PUBLICATIONS 2,688 CITATIONS

SEE PROFILE



Tarek Mohamed

Al-Azhar University

48 PUBLICATIONS 365 CITATIONS

SEE PROFILE



Todor K Gounev

University of Missouri - Kansas City

77 PUBLICATIONS 576 CITATIONS

SEE PROFILE

Conformational stability, r_0 structural parameters, barriers to internal rotation, ab initio calculations, and vibrational assignment for 2,2-difluoroethanol

James R. Durig · Arindam Ganguly ·
Gamil A. Guirgis · Stephen Bell ·
Tarek A. Mohamed · Todor K. Gounev

Received: 12 November 2008 / Accepted: 25 February 2009 / Published online: 19 March 2009
© Springer Science+Business Media, LLC 2009

Abstract The infrared spectra (4,000–30 cm^{-1}) of the gas and solid and the Raman spectrum of liquid 2,2-difluoroethanol as well as variable temperature infrared spectra of krypton/xenon solutions have been recorded. From all these data, two (Gg and Tg) out of the five possible stable conformers have been confidently identified. The order of the stabilities has been predicted to be $\text{Gg} > \text{Tg} > \text{Gt} > \text{Gg}' > \text{Tt}$ by utilizing ab initio MP2 (full) and DFT (B3LYP method) calculations, where the first indicator (capital letter) is in reference to rotation around the C–C bond ($G = \text{gauche}$ or $T = \text{trans}$) and the second one (small letter) refers to the orientation of the hydroxyl group. The percentage of the minor conformer Tg, at ambient temperature, is estimated to be $(16 \pm 3\%)$. The optimized geometries, fundamental frequencies, infrared intensities, Raman activities, and depolarization values as well as centrifugal distortion constants have been obtained from ab initio and density functional theory calculations by utilizing a variety of basis

sets as well as those with diffuse functions. By utilizing the previously reported microwave rotational constants for two isotopomers of the Gg conformer combined with ab initio MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained. The determined heavy atom distances (\AA) for the Gg conformer are: $\text{C}_1\text{--C}_2 = 1.510(3)$, $\text{C}_2\text{--F}_4 = 1.371(3)$, $\text{C}_2\text{--F}_5 = 1.362(3)$, $\text{C}_1\text{--O}_3 = 1.412(3)$ \AA and angles $\angle \text{O}_3\text{C}_1\text{C}_2 = 111.0(5)$, $\angle \text{F}_4\text{C}_2\text{C}_1 = 108.8(5)$, $\angle \text{F}_5\text{C}_2\text{C}_1 = 109.8(5)$, $\tau \text{F}_4\text{C}_2\text{C}_1\text{O}_3 = 63.5(5)$, $\tau \text{F}_5\text{C}_2\text{C}_1\text{O}_3 = 179.1(5)^\circ$. Barriers of internal rotation have been obtained and vibrational assignments for the Gg and Tg conformers are given. The five predicted centrifugal distortion constants compared to the experimental values are in reasonable agreement except for Δ_K , which appears to be in error. The results are discussed and the structural parameters compared to the corresponding ones for 2-fluoroethanol and 2,2,2-trifluoroethanol where those for the latter molecule have been redetermined. The currently determined heavy atom parameters are quite different from the earlier assumed values, which led to poor values of the six adjusted parameters.

Taken from the thesis of Arindam Ganguly, which will be submitted in partial fulfillment of the Ph.D. degree.

J. R. Durig (✉) · A. Ganguly · T. K. Gounev
Department of Chemistry, University of Missouri–Kansas City,
Kansas City, MO 64110, USA
e-mail: durigj@umkc.edu

G. A. Guirgis
Department of Chemistry and Biochemistry, College
of Charleston, Charleston, SC 29424, USA

S. Bell
Department of Physics, University of Dundee,
Dundee DD1 4HN, Scotland, UK

T. A. Mohamed
Department of Chemistry, Al-Azhar University,
Nasr City, Cairo, Egypt

Keywords Infrared and Raman spectra ·
 r_0 structural parameters ab initio calculations ·
Conformational stabilities · 2-Fluoroethanol ·
2, 2-Difluoroethanol · 2, 2, 2-Trifluoroethanol

Introduction

There has been recent interest [1] in the global warming potentials of the three 2-fluoroethanols as well as the atmospheric gas-phase degradation. Additionally there has been an investigation [2] of the adsorption and thermal decomposition of 2,2-difluoroethanol, $\text{CF}_2\text{H--CH}_2\text{OH}$, on a

high surface area of Al_2O_3 where infrared studies were utilized in the $4,000\text{--}1,000\text{ cm}^{-1}$ range, to identify the adsorption/decomposition process. The partially fluorinated alcohols are potential alternatives for CFCs and HCFCs, so the vibrational spectrum of 2,2-difluoroethanol is of scientific interest where the most comprehensive vibrational study [3] was reported 30 years ago prior to the use of ab initio calculations to support such studies. The 2,2-difluoroethanol molecule is also structurally interesting since there are five energetically different nonequivalent conformers inter convertible by rotation about the C–C or the C–O bonds, which are indicated by Gg, Gg', Gt, Tg, and Tt where the capital letter indicates *gauche* or *trans* orientation around the C–C bond and the lower case letter refers to the orientation of the hydroxyl moiety. However, from a microwave investigation [4] of this molecule only the spectrum of the Gg conformer was identified and assigned and it was concluded that if other conformations coexist with this conformer, their concentrations could not exceed $\sim 5\%$ at -25°C . As a continuation of our interest [5–7] in the vibrational spectra and conformational stabilities of alcohols, we initiated a spectral investigation of 2,2-difluoroethanol.

We have recorded the infrared spectra of the gas, krypton/xenon solutions at variable temperature, and solid along with the Raman spectrum of the liquid. To support the vibrational study, we have carried out ab initio calculations at the MP2 level with full electron correlation by the perturbation method as well as DFT calculation using the B3LYP method utilizing a variety of basis sets as well as those with diffuse functions. Additionally we were interested in the structural parameters for comparison to those of other 2-fluoroethanols, which we have obtained by combining ab initio calculations with previously reported [4] microwave rotational constants. The results of this spectroscopic and theoretical study are reported herein.

Experimental

The 2,2-difluoroethanol sample was purchased from Alfa Aesar Co., Ward Hill, MA with a stated purity of 97%. Further purification was carried out with a low-temperature, low-pressure vacuum fractionation column.

The mid-infrared spectra of gaseous 2,2-difluoroethanol were obtained using a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Nichrome wire source, a Ge/CsI beam splitter, and a DTGS detector. The spectrum of the gas was obtained by using a 10-cm cell fitted with CsI windows. The resolution used to obtain the spectra of the gas was 0.5 cm^{-1} and a typical spectrum is shown in Fig. 1a.

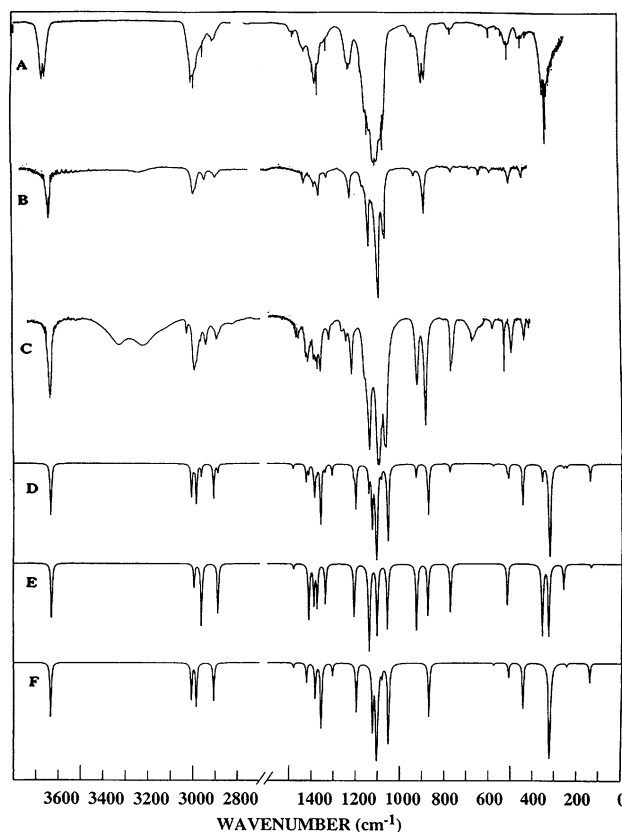


Fig. 1 Comparison of experimental and calculated infrared spectra of 2,2-difluoroethanol: (a) observed infrared spectrum of the gas; (b) xenon solution at -60°C ; (c) xenon solution at -60°C high concentration; (d) simulated infrared spectrum of the mixture of Gg and Tg conformer at 25°C with $\Delta H = 350\text{ cm}^{-1}$; (e) simulated infrared spectrum of Tg; and (f) simulated infrared spectrum of Gg

The mid-infrared spectra of the sample dissolved in liquefied xenon/krypton as a function of temperature were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter, and a DTGS detector. The temperature studies ranged from -55 to -150°C and were performed in a specially designed cryostat cell consisting of a 4-cm path length copper cell with wedged silicon windows sealed to the cell with indium gaskets. The complete system is attached to a pressure manifold to allow for the filling and evacuation of the cell. The cell is cooled by boiling liquid nitrogen and the temperature is monitored by two Pt thermoresistors. For each temperature investigated, 100 interferograms were recorded at 1.0 cm^{-1} resolution, averaged, and transformed with a boxcar truncation function. A typical spectrum at -60°C is shown in (Fig. 1b).

The far infrared spectrum of the gas was recorded on the previously described Perkin-Elmer model 2000 spectrometer. For the spectrum of the gas, the sample was contained in a 12-cm cell equipped with polyethylene windows. The spectra were recorded at a spectral resolution of 0.5 cm^{-1} ,

and typically 256 scans were used for both the sample and reference data to give a satisfactory signal-to-noise ratio.

The Raman spectra were recorded on a Spex model 1403 spectrophotometer equipped with a Spectra-Physics model 2017 argon ion laser operating on the 514.5-nm line. The laser power used was 1.5 W with a spectral bandpass of 3 cm^{-1} . The spectrum of the liquid was recorded with the sample sealed in a Pyrex glass capillary. The measurements of the Raman frequencies are expected to be accurate to $\pm 2\text{ cm}^{-1}$ and a typical spectrum is shown in Fig. 2.

The observed fundamental bands with their assignments are listed in Tables 1 and 2 for the Gg and Tg conformers, respectively, where the capital letter indicates *gauche* or *trans* orientation around the C–C bond and the lower case letter the similar orientation around the C–O bond.

AB initio calculations

The LCAO-MO-SCF restricted Hartree–Fock calculations were performed with the Gaussian-03 program [8] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the

simultaneous relaxation of all geometric parameters using the gradient method of Pulay [9]. A variety of basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [10] to the second-order MP2(full) as well as with the density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 3.

In order to obtain a complete description of the molecular motions involved in the fundamental modes of 2,2-difluoroethanol, a normal coordinate analysis has been carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program at the MP2(full) level with the 6-31G(d) basis set. The internal coordinates used to calculate the **G** and **B** matrices are given in Table 4 with the atomic numbering shown in Fig. 3. By using the **B** matrix [11], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, scaling factors of 0.93 for OH stretching, 0.88 for CH stretch, 0.60 for hydroxyl torsion and except for the heavy atom bends, 0.90 for all other coordinates were used, along with the geometric average of scaling factors for interaction force constants, to obtain the fixed scaled force field and resultant wavenumbers. A set of symmetry coordinates was used (Table 5) to determine the corresponding potential energy distributions (PEDs). A comparison between the observed and calculated wavenumbers, along with the calculated infrared intensities, Raman activities, depolarization ratios, and potential energy distributions for the Gg and Tg conformers, are given in Tables 1 and 2, respectively.

The infrared spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra. Infrared intensities determined from MP2(full)/6-31G(d) calculations were obtained based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were transformed with respect to normal coordinates by $(\partial\mu_u/\partial Q_i) = \sum (\partial\mu_u/\partial X_j)L_{ij}$, where Q_i is the i th normal coordinate, X_j the j th Cartesian displacement coordinate, and **L**_{ij} the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $[(N\pi)/(3c^2)] \cdot [(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$. In Fig. 1, a comparison of the experimental and simulated infrared spectra of 2,2-difluoroethanol is shown. Infrared spectrum of 2,2-difluoroethanol gas at ambient temperature (Fig. 1a) and the predicted infrared spectra for the pure Gg (Fig. 1f) and Tg (Fig. 1e) conformers, as well as the mixture (Fig. 1d) of the two conformers with relative concentrations calculated for the equilibrium mixture at ambient temperature by using the determined enthalpy difference of 350 cm^{-1} are presented.

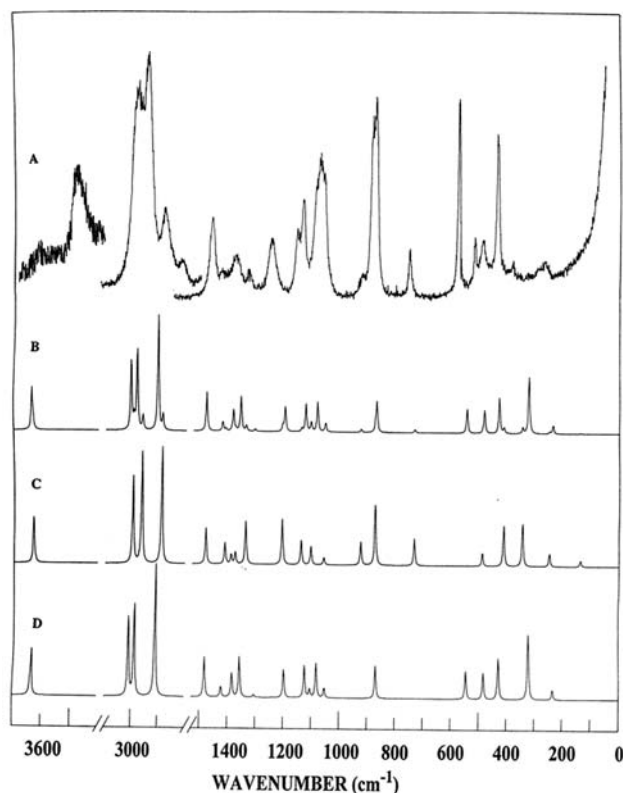


Fig. 2 Comparison of experimental and calculated Raman spectra of 2,2-difluoroethanol: (a) observed Raman spectrum of the liquid; (b) simulated Raman spectrum of the mixture of Gg and Tg conformer at 25 °C with $\Delta H = 350\text{ cm}^{-1}$; (c) simulated Raman spectrum of Tg; and (d) simulated Raman spectrum of Gg

Table 1 Vibrational wavenumbers of 2,2-difluoroethanol in the Gg conformer

Approx. description	MP2(full)/6-31G(d)	MP2(full)/6-31G(d) scaled ^a	IR ^b int.	Raman ^b act.	dp ^b ratio	IR gas	Xe soln	IR [3] matrix ^c	Raman liquid	PED ^d	Band Contour ^e		
											A	B	C
ν_1 O–H stretch	3,770	3,635	40.8	49.7	0.28	3,657	3,628	3,643	3,612	100S ₁	6	88	6
ν_2 CH ₂ antisym str	3,208	3,009	23.9	58.3	0.32	2,996	3,019	3,002	2,994	75S ₂ , 17S ₄	–	29	71
ν_3 C–H stretch	3,184	2,987	30.0	67.1	0.42	2,970	2,975	2,948	2,956	92S ₃	–	4	96
ν_4 CH ₂ sym stretch	3,101	2,909	25.2	92.7	0.15	2,911	2,933	2,893	–	81S ₄ , 19S ₂	14	19	67
ν_5 CH ₂ scissor	1,561	1,481	2.7	10.3	0.73	1,464	–	1,461	1,460	100S ₅	44	21	35
ν_6 CCH bend	1,499	1,422	11.6	2.6	0.60	1,414	1,416	1,420	1,424	31S ₆ , 43S ₆ , 13S ₁₅	16	72	12
ν_7 CCH wag	1,457	1,383	22.5	5.7	0.75	1,375	1,370	1,374	1,369	60S ₇ , 15S ₆ , 12S ₁₀	10	90	–
ν_8 COH bend	1,429	1,356	55.3	9.2	0.75	1,355	1,349	1,352	1,326	44S ₈ , 22S ₇ , 22S ₁₀	86	10	4
ν_9 CH ₂ wag	1,376	1,305	7.4	0.6	0.65	1,314	1,312	1,317	–	44S ₉ , 29S ₆ , 12S ₇	88	–	12
ν_{10} CH ₂ twist	1,261	1,197	35.2	5.5	0.74	1,210	1,209	1,213	1,244	49S ₁₀ , 19S ₈ , 10S ₁₆	82	12	6
ν_{11} CF ₂ sym stretch	1,184	1,123	58.5	5.7	0.72	1,135	1,129	1,156	1,153	32S ₁₁ , 32S ₁₅ , 14S ₆	9	80	11
ν_{12} CF ₂ antisym str	1,164	1,104	190.4	1.5	0.70	1,101	1,089	1,131	1,133	67S ₁₂ , 15S ₁₁	58	39	3
ν_{13} CH ₂ rock	1,134	1,081	5.7	5.9	0.23	1,086	1,075	1,089	–	26S ₁₃ , 31S ₁₄ , 17S ₁₆	–	13	87
ν_{14} C–O stretch	1,109	1,052	85.5	1.6	0.72	1,064	1,055	1,071	1,070	48S ₁₄ , 13S ₈	83	–	17
ν_{15} C–C stretch	915	868	40.4	4.2	0.32	868	874	876	872	19S ₁₅ , 34S ₁₃ , 19S ₁₁ , 12S ₁₂	5	95	–
ν_{16} CF ₂ wag	574	574	1.4	2.0	0.36	572	572	749	575	45S ₁₆ , 16S ₁₁ , 16S ₁₈	17	20	63
ν_{17} CCO bend	507	507	8.4	1.6	0.70	489	487	484	484	27S ₁₇ , 27S ₂₀ , 19S ₁₆	3	67	30
ν_{18} CF ₂ scissor	442	442	31.7	2.1	0.54	428	429	429	436	49S ₁₈ , 26S ₁₉ , 10S ₁₅	10	–	90
ν_{19} OH torsion	414	321	152.6	2.2	0.74	320	–	296	380	69S ₁₉ , 17S ₁₈	33	7	60
ν_{20} CF ₂ twist	246	245	2.0	0.2	0.73	245	–	240	268	51S ₂₀ , 42S ₁₇	52	48	–
ν_{21} CC torsion	149	141	11.2	0.0	0.71	136	–	(126)	–	97S ₂₁	52	33	15

^a Force constant scaling factors: 0.90 for heavy atom stretching, 0.88 for CH stretching, 0.93 for OH stretching, 0.90 for CH and OH bends, and 0.60 for hydroxyl torsion^b Infrared intensities (km/mol), Raman activities ($\text{\AA}^4/\text{u}$), depolarization ratios (dp)^c Infrared argon matrix data [3] and frequencies that are italicized are misassigned^d Potential energy distributions (PEDs) with contribution of less than 10% omitted^e Predicted infrared band contours calculated using rotational constants obtained from MP2(full)/6-31G(d)

Table 2 Vibrational wavenumbers of 2,2-difluoroethanol in the Tg conformer

Approx. description	MP2(full)/6-31G(d)	MP2(full)/6-31G(d) scaled ^a	IR ^b int.	Raman ^b act.	dp ^b ratio	IR gas	Xe soln.	Raman liquid	IR solid	PED ^c	Band contour ^d		
											A	B	C
ν_1 O–H stretch	3,765	3,631	41.6	48.1	0.26	3,655	3,634		3,281	100S ₁	1	52	47
ν_2 CH ₂ antisym str	3,196	2,998	14.2	64.1	0.43	2,984	2,984		3,025	75S ₂ , 25S ₄	1	92	7
ν_3 C–H stretch	3,161	2,965	51.6	81.6	0.23	2,942	2,957		2,995	99S ₃	23	–	77
ν_4 CH ₂ sym stretch	3,081	2,890	36.4	80.9	0.20	2,897	2,884	2,890	2,958	75S ₄ , 24S ₂	5	21	74
ν_5 CH ₂ scissor	1,560	1,480	3.0	9.4	0.73	1,459	1,450		1,450	100S ₅	71	–	29
ν_6 CCH bend	1,487	1,411	43.4	5.2	0.65	1,400	1,406		1,407	15S ₆ , 31S ₉ , 19S ₈	–	10	90
ν_7 CH ₂ wag	1,464	1,388	27.5	2.3	0.67	1,386	1,381		1,380	52S ₇ , 30S ₆	60	34	6
ν_8 CCH wag	1,448	1,374	30.3	2.8	0.72	–	1,364		1,365	38S ₈ , 21S ₁₀ , 11S ₉ , 10S ₁₃	36	60	4
ν_9 COH bend	1,409	1,337	26.9	9.8	0.73	1,336				43S ₉ , 29S ₆ , 21S ₇	90	–	10
ν_{10} CH ₂ twist	1,270	1,206	40.0	9.1	0.69	1,205	1,233		1,235	43S ₁₀ , 18S ₈ , 10S ₁₂	57	43	–
ν_{11} CF ₂ sym stretch	1,199	1,138	112.7	4.5	0.42	1,160	1,151		1,157	38S ₁₁ , 11S ₁₅ , 10S ₁₄	–	–	100
ν_{12} CH ₂ rock	1,162	1,102	67.4	3.3	0.67	–	1,132		1,135	39S ₁₂ , 23S ₁₄ , 19S ₁₃	–	100	–
ν_{13} CF ₂ antisym str	1,113	1,056	56.0	1.3	0.73	1,072	1,072		1,068	36S ₁₄ , 17S ₁₁ , 15S ₁₂	37	47	16
ν_{14} C–O stretch	974	924	58.1	3.3	0.75	923	917	917	9,13	54S ₁₃ , 34S ₁₂	13	77	10
ν_{15} C–C stretch	919	872	38.8	7.9	0.18	877			8,77	51S ₁₅ , 19S ₁₄ , 10S ₁₆	28	–	72
ν_{16} CF ₂ wag	771	771	35.0	2.9	0.55	750	747	750	7,62	35S ₁₆ , 29S ₁₇ , 21S ₁₁	83	2	15
ν_{17} CF ₂ scissor	513	513	28.3	0.8	0.74	515	519	518	519	72S ₁₈ , 10S ₁₆	55	5	40
ν_{18} OH torsion	420	325	68.1	2.0	0.75	334	650		680	50S ₁₉ , 39S ₂₀	63	30	7
ν_{19} CF ₂ twist	354	354	67.8	1.6	0.74	–	–	–	384	43S ₂₀ , 43S ₁₉	57	29	14
ν_{20} CCO bend	259	259	15.2	0.3	0.52	246			282	55S ₁₇ , 25S ₁₆	77	10	13
ν_{21} C–C torsion	136	136	1.9	0.1	0.74	127			166	95S ₂₁	16	14	70

^a Force constant scaling factors: 0.90 for heavy atom stretching, 0.88 for CH stretching, 0.93 for OH stretching, 0.90 for CH and OH bends, and 0.60 for hydroxyl torsion^b Infrared intensities (km/mol), Raman activities ($\text{\AA}^4/\text{u}$), depolarization ratios (dp)^c Potential energy distributions (PEDs) with contribution of less than 10% omitted^d Predicted infrared band contours calculated using rotational constants obtained from MP2(full)/6-31G(d)

Table 3 Calculated energies and energy differences for several conformations^a of 2,2-difluoroethanol by ab initio and hybrid DFT methods

Method/basis	Energy (E_h)	Energy differences ^b (cm ^{−1})			
	Gg	Tg	Gt	Gg'	Tt
HF/6-31G(d) ^c	−351.790651	626	705	960	1660
(τ , ρ)	(58.59, 66.10)	(183.23, 56.85)	(52.44, 172.17)	(56.45, −80.97)	(180, 180)
MP2(full)/6-31G(d)	−352.581708	493	971	1053	1679
(τ , ρ)	(58.83,61.51)	(183.71, 52.99)	(53.32, 174.12)	(57.78, −78.13)	(180, 180)
MP2(full)/6-311+G(d,p)	−352.906030	388	691 ^d	879 ^e	1321
MP2(full)/6-311+G(2d,2p)	−353.000976	464	690 ^d	846 ^e	1362
MP2(full)/6-311G(2df,2pd)	−353.088384	459	744 ^d	893 ^e	1413
MP2(full)/6-311+G(2df,2pd)	−353.105144	430	666 ^d	820 ^e	1303
MP2(full)/6-311++G(2df,2pd)	−353.105466	430	656 ^d	816 ^e	1295
MP2(full)/aug-cc-pVTZ	−353.125761	416	656	794 ^e	1305
MP2(full) Average cm ^{−1}		440 ± 35	725 ± 113	872 ± 87	1382 ± 137
B3LYP/6-31G(d)	−353.504832	493	947	971	1680
(τ , ρ)	(59.32, 59.65)	(185.28, 51.51)	(53.23, 175.16)	(58.31, −74.83)	(180, 180)
B3LYP/6-311+G(d,p)	−353.638347	450	721 ^d	847 ^e	1435
B3LYP/6-311G(2df,2pd)	−353.642508	475	780 ^d	854 ^e	2348
B3LYP/6-311+G(2df,2pd)	−353.657222	443	677 ^d	769 ^e	1340
B3LYP/6-311++G(2df,2pd)	−353.657355	440	672 ^d	766 ^e	1333
B3LYP/aug-cc-pVTZ	−353.670720	428	655 ^d	738 ^e	1281
B3LYP Average cm ^{−1}		455 ± 24	742 ± 110	824 ± 86	1570 ± 407

^a Conformation labels: capital letter refers to the torsional angle, τ = f OC₁C₂H*: G = *gauche*, T = *trans* or *ante*, C = *cis* or *syn*, and B = barrier; lower case letters refer to OH torsional angle, ρ = HOC₁C₂: g = *gauche* (60°), t = *trans* (180°), c = *cis* (0°), g' = *−gauche* (−60°), and s = skew (120°)

^b Energies of conformations relative to Gg

^c No minimum was found for some of these conformations with this method

^d The ρ (HOCC) = 174.12 was fixed at the MP2(full)/6-31G(d) value

^e The ρ (HOCC) = 78.13 was fixed at the MP2(full)/6-31G(d) value

Additionally the infrared spectrum of the xenon solutions (low concentration) is shown in Fig. 1b and there is excellent correspondence between this spectrum and that of the gas (Fig. 1a). However, with a significant increase in the concentration significant hydrogen bonding of the OH group is observed at 3,250–3,350 cm^{-1} as well as the OH torsional mode at 650 cm^{-1} (Fig. 1c). Nevertheless, the predicted spectrum is still in relatively good agreement with the experimental spectrum, which indicates the predicted scaled frequencies and intensities should provide good support for making the vibrational assignment.

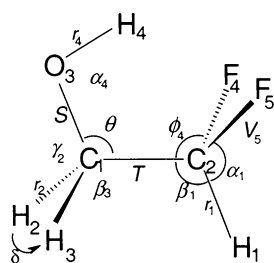
Also to further support the vibrational assignments, we have simulated the Raman spectra from the ab initio MP2(full)/6-31G(d) results. The evaluation of Raman activity by using the analytical gradient methods has been developed [12–15]. The activity S_j can be expressed as: $S_j = g_j (45\alpha_j^2 + 7\beta_j^2)$, where g_j is the degeneracy of the vibrational mode j , α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. To obtain the polarized Raman scattering cross sections, the polarizabilities are incorporated into S_j by

multiplying S_j with $(1 - \rho_j)/(1 + \rho_j)$, where ρ_j is the depolarization ratio of the j th normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the Gaussian 03 program were used together with a Lorentzian function to obtain the simulated Raman spectra. Comparison of experimental Raman spectra of the liquid (Fig. 2a) and the predicted Raman spectra for the pure Gg (Fig. 2d) and Tg (Fig. 2c) conformers, as well as the mixture (Fig. 2b) of the two conformers with relative concentrations calculated for the equilibrium mixture at 25 °C by using the determined enthalpy difference is shown. The predicted spectrum of the mixture should be compared to that of the Raman spectrum of the liquid at room temperature, although there may be some significant differences between the predicted and that obtained experimentally due to the hydrogen bonding in the liquid. Nevertheless, the intensities of several bands in the predicted spectrum are significantly different from the experimental spectrum of the scaled predicted frequencies of the Raman spectrum should aid in making the vibrational assignment.

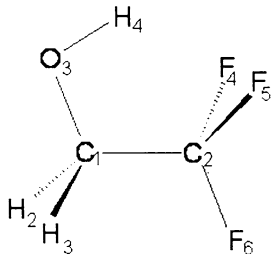
Table 4 Structural parameters (Å and degrees) for the two most stable conformers of 2,2-difluoroethanol

Structural parameters	Int. coord.	Tg conformer					
		HF/6-31G(d)	B3LYP/6-31G(d)	MP2(full)/6-31G(d)	MP2(full)/6-311+G(d,p)	Adjusted r_0 parameters ^a	Predicted r_0 parameters
C ₁ C ₂	<i>T</i>	1.5077	1.5171	1.5057	1.5098	1.510(3)	1.5108
C ₁ O	<i>S</i>	1.3935	1.4130	1.4162	1.4119	1.412(3)	1.4078
C ₂ F ₅	<i>V</i> ₄	1.3420	1.3648	1.3680	1.3617	1.362(3)	1.3733
C ₂ F ₄	<i>V</i> ₅	1.3495	1.3765	1.3784	1.3713	1.371(3)	1.3579
C ₂ H ₁	<i>r</i> ₁	1.0778	1.0948	1.0916	1.0906	1.090(2)	1.0923
C ₁ H ₂	<i>r</i> ₂	1.0864	1.1010	1.0978	1.0962	1.096(2)	1.0978
C ₁ H ₃	<i>r</i> ₃	1.0808	1.0934	1.0910	1.0905	1.091(2)	1.0912
OH ₄	<i>r</i> ₄	0.9481	0.9709	0.9729	0.9617	0.961(3)	0.9619
OC ₁ C ₂	<i>θ</i>	110.61	110.95	110.24	110.90	111.0(5)	112.53
F ₃ CC	<i>φ</i> ₄	109.61	109.87	109.70	109.78	109.8(5)	108.92
F ₄ CC	<i>φ</i> ₅	108.82	108.22	107.93	108.89	108.8(5)	111.2
H ₁ C ₂ C ₁	<i>β</i> ₁	113.55	113.63	114.02	113.81	113.8(5)	113.13
H ₂ C ₁ C ₂	<i>β</i> ₂	108.28	107.80	107.74	108.09	108.0(5)	107.56
H ₃ C ₁ C ₂	<i>β</i> ₃	109.39	109.55	109.89	108.94	108.9(5)	108.64
HOC ₁	<i>α</i> ₄	109.29	106.84	106.52	107.19	107.1(5)	107.4
H ₄ O ₃ C ₁ C ₂	<i>ρ</i>	66.10	59.65	61.54	63.06	64.3(5)	57.07
F ₄ C ₂ C ₁ O ₃		61.69	60.18	60.97	63.10	63.5(5)	60.44
F ₃ C ₂ C ₁ O ₃		179.12	178.00	178.36	179.39	179.1(5)	57.33
A		9300.3	9022.8	9036.8	9062.0	9070.8	7302.4
B		3832.9	3755.8	3785.8	3755.1	3744.7	4270.3
C		2924.0	2854.2	2875.6	2861.1	2856.8	3489.3
$ \mu_a $		0.433	0.222	0.319	0.606		0.091
$ \mu_b $		0.129	0.022	0.218	0.317		1.010
$ \mu_c $		0.068	0.004	0.074	0.109		2.706
$ \mu_{\text{tot}} $		0.457	0.223	0.393	0.692		2.890

^a For comparison rotational constants (MHz) and dipole moments (D): A = 9069.9, B = 3745.3, C = 2857.0 MHz, $|\mu_a| = 0.608$, $|\mu_b| = 0.282$, $|\mu_c| = 0.163$, $|\mu_{\text{tot}}| = 0.690$ D [4]



Atomic numbering of 2,2-difluoroethanol and the definition of internal coordinates.



Atomic numbering of 2,2,2-trifluoroethanol.

Fig. 3 Atomic numbering of 2,2,2-trifluoroethanol and 2,2-difluoroethanol including internal coordinates**Table 5** Symmetry coordinates for vibrations of 2,2-difluoroethanol adapted for the Gg conformer

Description ^a	Symmetry coordinate
O–H stretch	$S_1 = r_4$
CH ₂ antisymmetric stretch	$S_2 = r_2 - r_3$
C–H stretch	$S_3 = r_1$
CH ₂ symmetric stretch	$S_4 = r_2 + r_3$
CH ₂ scissors	$S_5 = (\sqrt{6} + 2)\delta - \beta_2 - \beta_3 - \gamma_2 - \gamma_3(\sqrt{6} - 2)\theta$
CCH bend	$S_6 = 2\beta_1 - \alpha_1 - \alpha_2$
CCH wag	$S_7 = \alpha_1 - \alpha_2$
COH bend	$S_8 = \alpha_4$
CH ₂ wag	$S_9 = \beta_2 + \beta_3 - \gamma_2 - \gamma_3$
CH ₂ twist	$S_{10} = \beta_2 - \beta_3 - \gamma_2 + \gamma_3$
CF ₂ symmetric stretch	$S_{11} = V_4 + V_5$
CF ₂ antisymmetric stretch	$S_{12} = V_4 - V_5$
CH ₂ rock	$S_{13} = \beta_2 - \beta_3 + \gamma_2 - \gamma_3$
C–O stretch	$S_{14} = S$
C–C stretch	$S_{15} = T$
CCF ₂ deformation	$S_{16} = \varepsilon + \phi_4 + \phi_5 - \beta_1 - \alpha_1 - \alpha_2$
CCO bend	$S_{17} = (\sqrt{6} + 2)\theta - \beta_2 - \beta_3 - \gamma_2 - \gamma_3 - (\sqrt{6} - 2)\delta$
CF ₂ scissors	$S_{18} = 2\varepsilon - \phi_4 - \phi_5$
OH torsion	$S_{19} = \rho$
CF ₂ twist	$S_{20} = \phi_4 - \phi_5$
CC torsion	$S_{21} = \tau$

^a Not normalized

Structural parameters

We have [16] shown that ab initio MP2(full)/6-311+G(d,p) calculations predict the r_0 structural parameters for more than fifty carbon–hydrogen distances better than 0.002 Å compared to the experimentally determined values from isolated CH stretching frequencies, which are compared [17] to previously determined values from earlier microwave studies. Thus, all of the carbon–hydrogen parameters can be taken from the MP2(full)/6-311+G(d,p) predicted values for 2,2-difluoroethanol. Also, we have found [18] that we can obtain good structural parameters by adjusting the structural parameters from the ab initio calculations to fit the rotational constants obtained from the microwave experimental data. In order to reduce the number of independent variables, the structural parameters are separated into sets according to their types. Bond lengths in the same set keep their relative ratio, which results in only three heavy atoms distances for 2,2-difluoroethanol. Also, the bond angles and torsional angles in the same set keep their differences in degrees, which result in angles to be determined. This assumption is based on the fact that the errors from ab initio calculations are systematic. Therefore, it should be possible to obtain “adjusted r_0 ” structural parameters for the Gg conformer of 2,2-difluoroethanol by utilizing the six previously reported [4] microwave rotational constants.

As can be seen from the data in Table 4, the MP2(full)/6-311+G(d, p) predicted parameters provided rotational constants that differ by maximum of 7.9 MHz too small for the *A* rotational constant and too large by 9.8 and 4.1 MHz for the *B* and *C* rotational constants, respectively. Therefore, only minor changes need to be made for the heavy atom distances as well as for the angles. With these minor changes, the six rotational constants reported previously [4] are fit to better than 1 MHz (Table 6) with the adjusted r_0 parameters listed to only four significant figures when comparing the ab initio predicted values with the experimental uncertainties in parenthesis with those for the CH distances of ± 0.002 Å and the heavy atom distances of ± 0.003 Å. The uncertainties in the angles are probably larger, and we estimate them to be $\pm 0.5^\circ$. Therefore, it is believed that the determined parameters as obtained are as good as can be determined in the gas phase by microwave data or by an electron diffraction study.

The structural parameters are also predicted for the second most stable conformer, Tg, by adjusting the heavy atom parameters by the same amounts as obtained for the Gg conformer to the predicted values from the MP2(full)/6-311+G(d, p) ab initio calculations. These parameters are also listed in Table 4. The rotational constants obtained from these predicted structural parameters should make it relatively easy to identify and assign the transitions of this

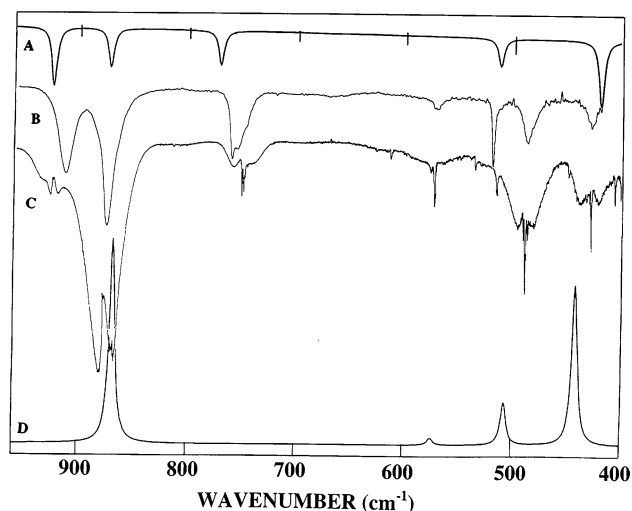
Table 6 Comparison of rotational constants obtained from ab initio MP2(full)/6-311+G(d,p) prediction structural parameters adjusted by rotational constants obtained from microwave spectra for 2-fluoroethanol, 2,2-difluoroethanol, and *gauche* 2,2,2-trifluoroethanol

Conformer	Isotopomers	Rotational constants	Observed	Calculated	Δ
<i>Gauche</i> ^a	CFH ₂ CH ₂ OH	A	15875.18	15876.06	0.88
		B	5409.26	5409.24	0.02
		C	4525.83	4526.72	0.89
Gg ^b	CF ₂ HCH ₂ OH	A	9069.93	9070.84	0.91
		B	3745.27	3744.77	0.50
		C	2857.01	2856.89	0.12
Gg ^b	CF ₂ HCH ₂ OD	A	8953.16	8952.21	0.95
		B	3640.08	3640.61	0.53
		C	2785.95	2786.08	0.13
<i>Gauche</i> ^c	CF ₃ CH ₂ OH	A	5319.90	5320.15	0.25
		B	2828.50	2827.54	0.96
		C	2796.30	2795.68	0.62
<i>Gauche</i> ^c	CF ₃ CH ₂ OD	A	5275.60	5275.26	0.34
		B	2754.30	2755.24	0.94
		C	2722.80	2723.42	0.62

^a Experimental rotational constants Ref. [24]; calculated values from structural parameters in Table 10

^b Experimental rotational constants Ref. [4]; calculated values from structural parameters in Table 4

^c Experimental rotational constants Ref. [20]; calculated values from structural parameters in Table 9

**Fig. 4** Mid-infrared spectra of 2,2-difluoroethanol gas: (a) simulated infrared spectrum of Tg; (b) xenon solution at $-60\text{ }^{\circ}\text{C}$; (c) observed infrared spectrum; and (d) simulated infrared spectrum of Gg

conformer in the microwave spectrum. This conformer is predicted to have a relatively large dipole (2.71 D) $|\mu_c|$ dipole component, which should make the microwave spectrum, have considerable intensity even with the small

amount present at $-77\text{ }^{\circ}\text{C}$. Therefore, an additional microwave investigation of 2,2-difluoroethanol would be of interest.

Conformational stability and barriers to internal rotation

In the most extensive vibrational study of 2,2-difluoroethanol [3], the infrared spectra of the normal species and OD isotopomer were investigated in both argon and nitrogen matrices and the Raman spectrum of the normal species as a liquid were also recorded. Vibrational assignments were provided for both isotopomers, which were supported by a Urey–Bradley force field calculation with the initial force field transferred from an earlier study of 2-fluoroethanol [19]. From careful studies of both the OH stretch and the OH torsion in both matrices, no change in the intensities was observed from the infrared radiation. From these observations, it was concluded that any noted differences between the spectral observations in the argon and nitrogen matrices was due to site effects rather than conformational interconversion. Thus, from the earlier vibrational study [3], no evidence was found for a second conformer.

In Fig. 4, a portion of the predicted infrared spectrum of the Gg conformer is shown along with the spectrum of the gas for comparison. This spectrum clearly shows the A-type band at 750 cm^{-1} where no band is predicted for the Gg conformer near this frequency since the CF₂ deformation is observed at 572 cm^{-1} and the CC stretch at 868 cm^{-1} with no fundamentals predicted between them. However, for the Tg conformer, an A-type fundamental i.e., CF₂ deformation, is predicted at 771 cm^{-1} with an intensity of 35.0 km/mol . Thus, the 750 cm^{-1} band can be confidently assigned as this fundamental for the Tg form. Additionally on the higher wavenumber side of the 877 cm^{-1} band (CC stretch) for the Gg form, there is a well-defined B-type band at 923 cm^{-1} , which can also be confidently assigned as the CO stretch, which is predicted at 924 cm^{-1} with an intensity of 58.1 km/mol for the Tg conformer.

In addition to these two fundamentals, there are several other observed bands, which can be assigned to the Tg conformer but most of these bands are close to the fundamentals of the Gg form, so their contours and intensities cannot be confidently determined. Also it should be noted that many of the predicted fundamentals for the Tg conformer are very near to fundamentals for the Gg conformer, so they can only be assumed to be accidentally coincident. A good example is ν_{17} , which should give rise to a B(67%)/C(30%) hybrid for the Gg conformer with a predicted intensity of 8.4 km/mol , whereas the corresponding vibration for the Tg form is predicted to be 6 cm^{-1} higher

in frequency but with an $A(55\%)/C(40\%)$ hybrid band and a predicted intensity of 28.3 km/mol. There appears to be one band at 489 cm^{-1} with either a B/C or A/C contour but the intensity is significantly larger than 8.4 km/mol as predicted for the Gg form so it is most reasonable to assign it as arising from both conformers although there is a relatively weak C -type band at 515 cm^{-1} , which could be ν_{17} for the Tg conformer. Since there is no combination or overtone bands for the Gg conformer for which this band can be assigned we have assigned it as ν_{17} of the Tg form. The other weak band at 535 cm^{-1} can readily be assigned as the $\nu_{21} + \nu_{18}$ combination band of the Gg conformer. From judicious assignments for the lower frequency spectral region, which is most sensitive for conformer identification, there is clear spectral evidence in the region from 400 to 960 cm^{-1} (Fig. 4), which provides convincing data that there is a second conformer present at ambient temperature in the gas phase of the 2,2-difluoroethanol molecule.

With conclusive evidence for a second conformer, our attention was turned to the determination of the enthalpy difference between them. Firstly, estimates of ΔH were obtained from measured relative intensities of pairs of bands at a single temperature of $-60\text{ }^{\circ}\text{C}$ combined with the ε values predicted from the ab initio calculations. We chose the 874 cm^{-1} for the Gg conformer while knowing that it had a small contribution to its intensity from the Tg form. The 917 cm^{-1} band was selected for the Tg conformer, which gave a ΔH value of 299 cm^{-1} . The areas of a second pair at 572 cm^{-1} (Gg) and 519 cm^{-1} (Tg) were measured and the determined ΔH value was 307 cm^{-1} . The areas of the third pair of bands at 487 cm^{-1} (Gg) and 519 cm^{-1} (Tg) at $-60\text{ }^{\circ}\text{C}$ as well as $-55\text{ }^{\circ}\text{C}$ gave ΔH values of 295 and 302 cm^{-1} , respectively. These results were taken to indicate a lower limit of 300 cm^{-1} for the enthalpy difference between these two conformers.

Secondly, we measured the areas under the contours of the 868 cm^{-1} (Gg) and 923 cm^{-1} (Tg) bands of the gas at room temperature and obtained a ΔH value of 419 cm^{-1} . This value is considerably higher but it could not be quite as accurately determined and it should not be affected by dimer formation or from the xenon solvent.

Thirdly, we utilized variable temperature studies of the infrared spectrum of xenon solutions with special attention to the 747 and 917 cm^{-1} bands of the Tg form and the 874 cm^{-1} band of the Gg form with the small contribution of the Tg conformer. There was a pronounced low frequency shoulder on the 747 cm^{-1} band, which grew significantly as the temperature was lowered from -55 to $-95\text{ }^{\circ}\text{C}$. The appearance of the shoulder was assumed to be the result of a dimer or higher oligomers, which were more persistent with decreasing temperature. The $874/917\text{ cm}^{-1}$ pair had a significant change of their relative intensities

from -55 , -60 , -65 , $-70\text{ }^{\circ}\text{C}$ so we took their change of intensity over this range to obtain a value of ΔH while knowing the 874 cm^{-1} included a very weak fundamental from the Tg form, which still should give a good estimate of the enthalpy difference. The ΔH value obtained was $332 \pm 17\text{ cm}^{-1}$, which is consistent with the values obtained from the measurements at one temperature.

Finally, we measure the areas under the 747 cm^{-1} (Tg) band over the temperature range from -55 to $-70\text{ }^{\circ}\text{C}$ and compared it to the area under the 874 cm^{-1} band and obtained ΔH above 400 cm^{-1} but with a large uncertainty. By taking all of these data in consideration, we believe the value of $350 \pm 50\text{ cm}^{-1}$ ($4.19 \pm 0.60\text{ kJ/mol}$) for ΔH between the Gg and Tg conformers is consistent with the spread of values. This value gives the amount of the Tg form present at ambient temperature at $16 \pm 3\%$. This value can be compared to the ab initio predicted values that ranged from a low of 388 cm^{-1} to a high of 464 cm^{-1} for the MP2 (full) calculations excluding the small 6-31G(d) basis set, which gives an average value of $431 \pm 28\text{ cm}^{-1}$.

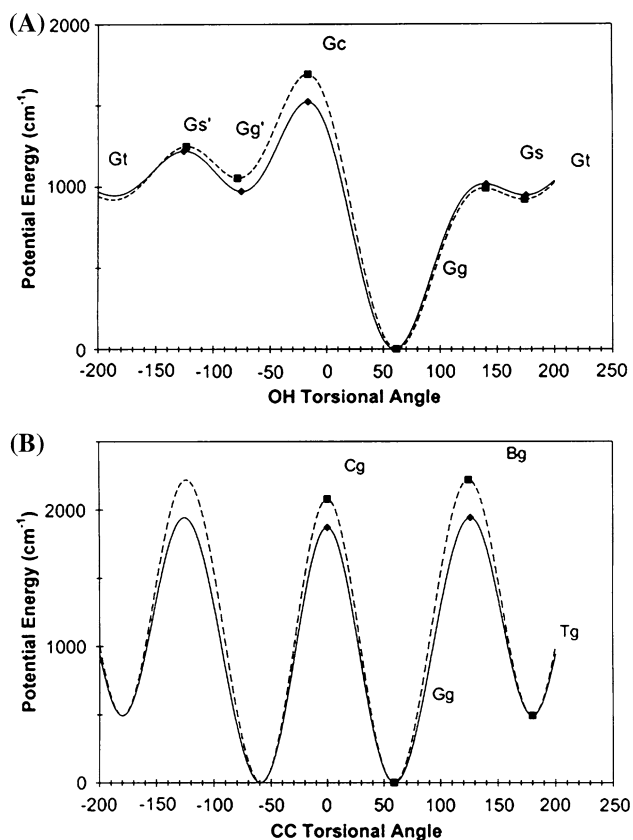
The torsional potential has been predicted for both the internal rotation of the hydroxyl torsion and around the carbon–carbon bond. We have used both ab initio MP2 (full) and density hybrid function by the B3LYP method by using the 6-31G(d) basis set since we have found that it gives good predictions for the methyl group. We have calculated the energies of the transition states relative to the various stable conformers. These predicted energies and the angles for the transition states as well as the various stable conformers are listed in Table 7. These data give the potential function for the OH torsional mode as shown in Fig. 5a and these predictions indicate that there should be three bound states of this torsion mode for the Gg form from which it should be possible to see the fundamental with one “hot band” for the OH torsion. In Fig. 5b, the potential for the carbon–carbon rotation is shown with the barrier of $\sim 2,000\text{ cm}^{-1}$ to the Tg form. The potential barriers are slightly lower from the B3LYP calculations compared to those from the MP2 (full) calculations but not significantly different.

Vibrational assignment

A reasonably definitive assignment based on infrared spectra of argon and nitrogen matrices was reported previously [3], which was supported by initial force constants obtained [19] earlier. Thus, there are only three fundamentals, which are clearly incorrectly assigned in the earlier study with one of them being the 750 cm^{-1} band, which is clearly due to the Tg but was previously assigned as the CF_2 bend. This CF_2 bend is assigned at 572 cm^{-1} , which was previously observed in the matrix spectrum but

Table 7 Calculated energies and energy differences for transition states^a of 2,2-difluoroethanol by ab initio and hybrid DFT methods

Method	HF/3-21G		HF/6-31G(d)		MP2(full)/6-31G(d)		B3LYP/6-31G(d)	
Config.	ΔE	(τ , ρ)	ΔE	(τ , ρ)	ΔE	(τ , ρ)	ΔE	(τ , ρ)
Cg ^b	1973.7	(−8.84, 90.51)	1844.0	(−6.36, 82.32)	2076.7	(−6.39, 79.82)	1870.8	(−6.53, 77.84)
Bg ^{b,c}	2164.2	(124.23, 6.61)	2182.1	(125.18, 52.39)	2217.7	(124.45, 48.79)	1942.2	(125.98, 45.67)
Gc ^b	1989.0	(64.46, −20.11)	1630.9	(63.41, −15.43)	1691.5	(64.11, −16.30)	1521.5	(64.62, −16.23)
Gs ^b	830.5	(49.51, 141.00)	764.6	(48.51, 139.98)	989.5	(51.67, 140.26)	1015.5	(51.75, 140.52)
Gs ^b	1353.6	(51.60, −113.56)	1088.5	(55.71, −120.01)	1247.3	(57.06, −122.70)	1219.7	(57.00, −124.98)
Tc ^b	1580.7	(180, 0)	1282.8	(180, 0)	1183.7	(180, 0)	1181.6	(180, 0)
Ct ^d	859.2	(0, 180)	929.1	(0, 180)	1072.3	(0, 180)	984.3	(0, 180)
Bt ^d	2818.0	(123.43, 172.12)	2066.7	(122.77, 176.93)	2349.5	(122.25, 177.36)	2429.0	(122.46, 177.24)

^a Relative to various stable conformers and in cm^{−1}^b Relative to Gg^c A higher saddle point was found for HF/6-31G(d) only at (114.43°, −47.52°)^d Relative to Gt. Tt is 1438.8 cm^{−1} higher than Gt used for potential plot**Fig. 5** Predicted (dotted curve) from MP2(full)/6-31G(d) and (solid curve) from B3LYP/6-31G(d) calculation of the potential function governing the internal rotation of the (a) OH group from the Gg conformer and (b) CC torsion of the Gg conformer of 2,2-difluoroethanol

attributed to association. There is also incorrect assignment of the band at 1,156 cm^{−1} as the fundamental ν_{11} but there is no fundamental predicted between 1,123 and 1,197 cm^{−1} where the modes can be confidently assigned

at 1,135 and 1,210 cm^{−1}. Both of these bands were observed in the matrix spectrum but the 1,135 cm^{−1} band was assigned as ν_{12} but ν_{12} is predicted as one of the strongest band in the spectrum, which is clearly the 1,101 cm^{−1} band, which is approximately three times the intensity of the 1,135 cm^{−1} band, which we assigned as the ν_{11} fundamentals.

The third assignment for which we disagree with the earlier one [3] is the one for the carbon–hydrogen stretch (C₂–H), which was previously assigned [3] at 2,948 cm^{−1}, which appears to be low for this mode where there are two fluorine atoms on the carbon. We have assigned this mode at 2,970 cm^{−1}, which has a nearly pure C-type contour (predicted 96%) and the strongest band in the spectral region. The 2,942 cm^{−1} also has a C-type contour but relatively weak compared to the 2,970 cm^{−1} band, so it has been assigned to the Tg conformer since this vibration is predicted to have a frequency 22 cm^{−1} lower than the corresponding mode for the Gg form. There is some question whether ν_4 should be assigned at 2,911 cm^{−1} or at 2,897 cm^{−1}. We chose the higher frequency band since it was more consistent with the ab initio predicted value along with the fact that the 2,897 cm^{−1} band was more consistent with the predicted value for the corresponding mode for the Tg form. However, there is some support for the alternative assignment from the Raman spectrum of the liquid where the third Raman line is observed at 2,890 cm^{−1}, which is consistent with the expected shift in going from the gas to the liquid.

It is expected that there is significant association in the liquid state with probably a preponderance of the dimer but the observed Raman lines for most of the fundamentals have frequencies, which are not significantly different for the corresponding modes in the gaseous state (Table 1). There is also support for the presence of the second

conformer in the Raman spectrum of the liquid where the 750 and 917 cm^{-1} band are clearly observed (Fig. 2).

There is significant mixing of the normal modes as indicated by the P.E.D.s. Ten of the 21 vibrations have significant contributions from three different modes and one, the C–C stretch has contributions from four symmetry coordinates. In fact, there is more contribution from the CH_2 rock (34%) with the CF_2 symmetric stretch (32%) at 1,135 cm^{-1} . Therefore, the approximate description in some cases is more for bookkeeping than indicating the major atom motions. Nevertheless, there are only three vibrations where there is more contribution than indicated by the approximate description and two where there is equal amounts. Thus, the approximate description can be useful for comparison of vibrational modes to other similar molecules.

Discussion

By the utilization of ab initio calculations to predict the infrared spectrum of 2,2-difluoroethanol the CF_2 wag for the Tg conformer is predicted at 771 cm^{-1} without any scaling and observed at 750 cm^{-1} . There is no fundamental predicted for the Gg form between the CF_2 wag at 572 cm^{-1} to the CC stretch at 868 cm^{-1} so there can be no question that a second conformer is present at ambient temperature particularly when many of the other fundamentals for the Tg form are observed in the infrared spectrum of the gas. This conformer is also predicted from the ab initio and density functional theory calculations. Based on the determined enthalpy difference of $350 \pm 50 \text{ cm}^{-1}$ the amount of the Tg, which is present at the ambient temperature is $16 \pm 3\%$. However, at -77°C the predict amount is $6 \pm 3\%$, which is consistent with the value of 5% as upper limit for a second conformer reported from the microwave study [4]. Based on the ab initio and density functional predicted enthalpy difference low value of $725 \pm 113 \text{ cm}^{-1}$ to high value of $1382 \pm 137 \text{ cm}^{-1}$ for the other three possible conformers there was no reason to search for the third conformer, Gt (Table 3) even with moderately increased temperatures.

The assignment of the fundamentals was greatly aided by the ab initio predicted intensities and the band contours, particularly since many of the corresponding fundamentals for the two conformers have different predicted contours even though their frequencies were similar to those for the Gg conformer (Fig. 6). To obtain information on the species present in the solid, we recorded both the mid and far infrared spectrum. As can be observed from the spectrum shown in Fig. 7, there are clearly six well-defined bands from 100 to 300 cm^{-1} with significantly different frequencies for the two bands observed at 519 and 384 cm^{-1}

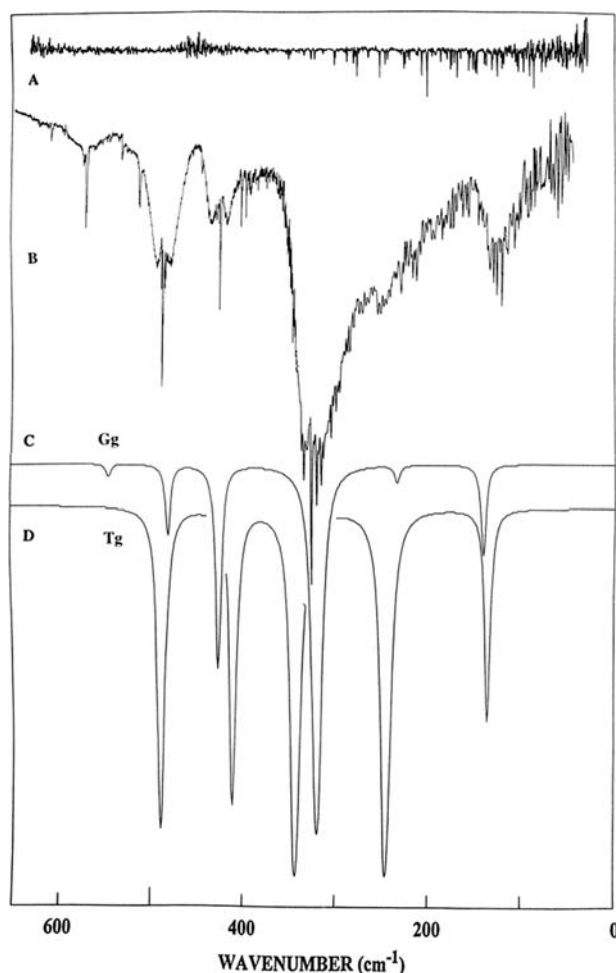


Fig. 6 Low frequency spectra (50–650 cm^{-1}) of: (a) infrared of water vapor; (b) infrared of 2,2-difluoroethanol gas; (c) simulated infrared spectrum of Tg; and (d) simulated infrared spectrum of Gg

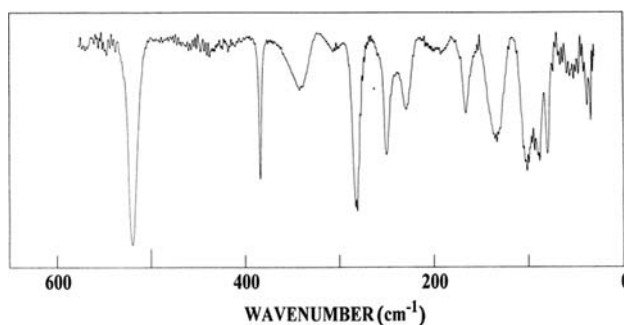


Fig. 7 Low frequency (0–650 cm^{-1}) spectrum of solid 2,2-difluoroethanol

compared to the observed frequencies for the three fundamentals ν_{17} , ν_{18} , ν_{19} observed from the spectrum of the gas as well as very similar values for these fundamentals from the Raman spectrum of the liquid. Thus, the spectrum of the solid indicates very strong interactions so spectral data in this physical state are of little value for making

assignments for the fundamentals in the fluid states in this region. The bands from 133 cm^{-1} to 341 cm^{-1} are associated with bands of the dimer.

It should be noted that we were able to assign most of the fundamentals for a second conformer with only $16 \pm 3\%$ present but there is a reasonable explanation. The Tg form is the stable form in solid phase (Fig. 8). From these data, it was possible to identify some very weak infrared bands in the gas phase as fundamentals for the Tg

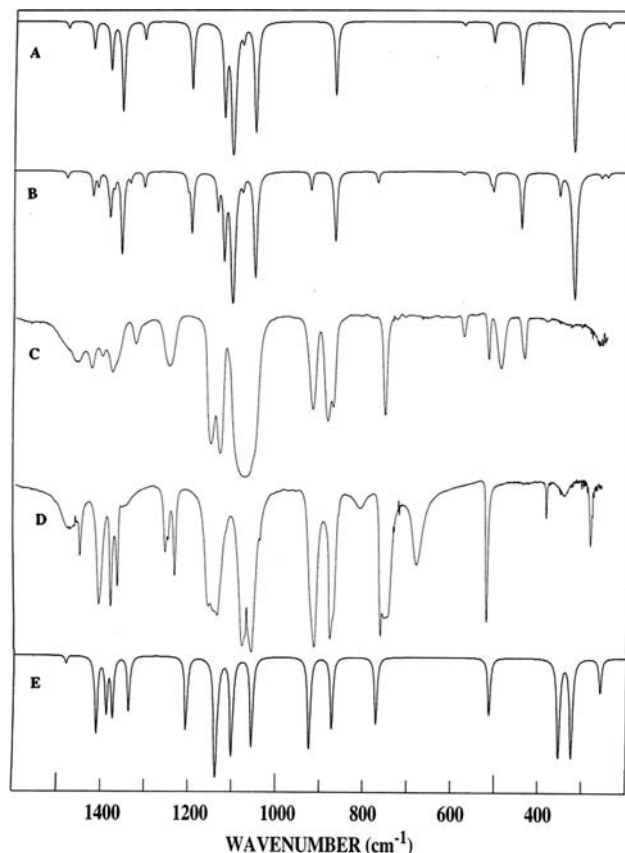


Fig. 8 Comparison of experimental and calculated infrared spectra of 2,2-difluoroethanol: (a) simulated infrared spectrum of Gg; (b) simulated infrared spectrum of the mixture of Gg and Tg conformer at $25\text{ }^{\circ}\text{C}$ with $\Delta H = 350\text{ cm}^{-1}$; (c) amorphous solid; (d) solid annealed; and (e) simulated infrared spectrum of Tg

form rather than combination modes of the Gg conformer. For the Tg form, there is a pronounced effect on the CF_2 modes where CF_2 is shifted to 750 cm^{-1} , whereas this mode is observed at 572 cm^{-1} for the Gg conformer. The other CF_2 bands are also significantly affected and the mixing is also significantly different. For example, the band at 489 cm^{-1} for the Gg form is assigned as the CCO bend (27%) with significant contributions from S_{20} (27%) and S_{16} (19%), whereas for the Tg form the CCO bend (55%) is assigned at 246 cm^{-1} with a contribution of S_{16} (25%), which is the CF_2 twist. Thus, these major differences along with the very good predictions of the band contours and intensities made it possible to assign 18 of the 21 fundamentals for the Tg conformer.

In the microwave study, all five of the normally determined centrifugal distortion constants were obtained for the normal species and only Δ_J and Δ_{JK} for the OD isotopomer. We have predicted these parameters by utilizing the force constants from both the MP2 (full) and B3LYP calculations with both the 6-31G(d) and 6-311+G(d, p) basis sets and compared them to the experimentally determined values (Table 8). There is good agreement for Δ_J for the normal species and satisfactory results for Δ_{JK} but those for δ_J and δ_K differ by nearly a factor of two. The very large experimental value of $50.0(21)\text{ kHz}$ for Δ_K is probably an error since we were not able to obtain this value from the frequencies for the transitions given in reference [4]. The values of Δ_J and Δ_{JK} for the OD isotopomer are much different from the predicted values and are also expected to be poorly determined since they should have relatively similar values to those for the corresponding distortion constants for the normal isotopomer.

For comparison of the structural parameters obtained in this study for 2,2-difluoroethanol, we first tried the reported [20] values for *gauche* 2,2,2-trifluoroethanol but soon found that the assumed parameter for the C–C bond was much too short by at least 0.020 \AA since it was transferred from the carbon–carbon distance for 1,1,1-trifluoroethane [21]. With the OH group placed on the other end of the CF_3CH_3 molecule, the CC bond of trifluoroethanol is

Table 8 Quadratic centrifugal distortion constants (kHz) for isotopomers of $\text{CHF}_2\text{CH}_2\text{OH}$ and $\text{CHF}_2\text{CH}_2\text{OD}$

	$\text{CHF}_2\text{CH}_2\text{OH}$					$\text{CHF}_2\text{CH}_2\text{OD}$				
	MP2(full)/6-31G(d)	MP2(full)/6-311+G(d,p)	B3LYP/6-31G(d)	B3LYP/6-311+G(d,p)	Exp. ^a	MP2(full)/6-31G(d)	MP2(full)/6-311+G(d,p)	B3LYP/6-31G(d)	B3LYP/6-311+G(d,p)	Exp. ^a
Δ_J	0.864	0.875	0.923	0.934	0.945(95)	0.882	0.891	0.948	0.956	0.46(14)
Δ_{JK}	6.43	6.72	7.01	6.78	5.84(43)	5.76	6.01	6.27	5.92	9.21(78)
Δ_K	1.88	1.29	1.35	1.52	50.0(21)	2.06	1.52	1.60	1.82	–
δ_J	0.196	0.202	0.214	0.219	0.116(22)	0.199	0.205	0.218	0.223	–
δ_K	3.91	4.11	4.34	4.22	7.51(56)	3.61	3.81	4.01	3.88	–

^a Values taken from Ref. [4]

Table 9 Structural parameters (\AA and $^\circ$) for *gauche* 2,2,2-trifluoroethanol

Structural parameters	MP2(full)/6-311+G(d,p)	Fit I ^a	Fit II ^a	Fit III ^a	Adjusted r_0 parameters ^b
$r(\text{C}_1\text{--C}_2)$	1.513	1.490*	1.490*	1.490*	1.513(5)
$r(\text{C}_1\text{--O})$	1.405	1.430*	1.430*	1.430*	1.406(5)
$r(\text{O--H})$	0.962	0.960*	0.960*	0.960*	0.962(2)
$r(\text{C--H})$	1.089	1.100*	1.100*	1.100*	1.089(2)
$r(\text{C--H}_2)$	1.095	1.100*	1.100*	1.100*	1.095(2)
$r(\text{C}_2\text{--F}_4)$	1.350	1.3432(2)	1.344(1)	1.349(4)	1.348(5)
$r(\text{C}_2\text{--F}_5)$	1.336	1.3432(2)	1.344(1)	1.349(4)	1.336(5)
$r(\text{C}_2\text{--F}_6)$	1.343	1.3432(2)	1.340*	1.327(11)	1.343(5)
$\angle(\text{COH})$	107.8	105.4*	105.4*	105.4*	107.8(5)
$\angle(\text{CCO})$	111.8	112.3*	112.3*	112.3*	112.4(5)
$\angle(\text{F}_4\text{CC})$	110.5	111.871(5)	112.1(1)	112.6(4)	110.6(5)
$\angle(\text{F}_5\text{CC})$	112.5	111.871(5)	112.1(1)	112.6(4)	112.7(5)
$\angle(\text{F}_6\text{CC})$	110.5	110.440(4)	110.5(1)	110.7(2)	110.6(5)
$\tau(\text{F}_4\text{CCO})$	59.2	60.23(1)	60.0*	0.0*	59.2(5)
$\tau(\text{F}_5\text{CCO})^c$	300.7	299.77(1)	300.0*	300.0*	−60.7(5)
$\tau(\text{F}_6\text{CCO})$	178.3	180.0*	180.0*	180.0*	178.3(5)
$\tau(\text{CCOH})$	63.6	68.97(6)	68.7(5)	69.0(5)	63.6(5)
<i>A</i>	5309.18		5319.9		5320.15
<i>B</i>	2833.50		2828.5		2827.53
<i>C</i>	2802.90		2796.3		2795.67

^a Ref. [20]; asterisk indicates assumed values

^b This study

^c $\tau(\text{F}_5\text{CCO}) = 360^\circ$
 – $\tau(\text{F}_4\text{CCO})$

expected to be much longer. Additionally, the assumed value for the CO distance, which was taken from the value for this parameter for ethanol [22] was too long by at least 0.020 \AA . Again the CF_3 group is expected to shorten the CO bond relative to its value for ethanol so the assumed parameters were expected to be far from the actual values for these two parameters in the trifluoroethanol. Also by using these assumed parameters as fixed parameters the determined values for the three CF bonds were expected to be rather poorly determined although the uncertainties were very small. Therefore, to be able to compare the structural parameters of trifluoroethanol to the corresponding ones of difluoroethanol, we re-evaluated the parameters by utilizing ab initio predicted values and adjusting them with the six microwave determined rotational constants [20]. The adjusted r_0 parameters obtained are listed in Table 9. These parameters reproduce the six reported [20] rotational constants to better than 1 MHz and it is believed that the heavy atom distances have uncertainties not more than 0.005 \AA or maybe even less. The predicted differences in the three CF distances should not have uncertainties more than 0.001 \AA among them although the actual distances overall for them may have the larger estimated value. The uncertainties in the CH distances are expected to be 0.002 \AA with all angle uncertainties of 0.5°. It is our assessment that these parameters for 2,2,2-trifluoroethanol as adjusted r_0 values are now well determined.

To complete the structural determinations of the fluoroethanols for comparison to the reported values [23, 24], we also obtained adjusted r_0 parameters by utilizing the previously determined [24] rotational constants for *gauche* 2-fluoroethanol to adjust the ab initio MP2(full)/6-311+G(d, p) predicted structural parameters. The resulting adjusted r_0 values are listed in Table 10 along with the r_g parameters from the electron diffraction studies [23]. By taking into account the uncertainties of the electron diffraction values, it is seen that there is excellent agreement. It is interesting to note that difference in the C–F distance is only 0.004 \AA although the r_g value has a listed uncertainty of 0.024 \AA . For the earlier microwave study [24] also by taking the lower end values of the r_g parameters for the C–C and C–O bond distances, there is again agreement with these values with the adjusted r_0 parameters. Also it should be noted that the assumed parameters for all but the two dihedral angles were taken from ethyl fluoride [25] and 2-chloroethanol [26] so they are in relatively good agreement if a reason uncertainty is transferred from these parameters as originally determined for these molecules. Therefore, we believe the adjusted r_0 parameters as reported herein are good to at least the values with the listed uncertainties and may be even better for the heavy atom distances.

Therefore, the reported trends for the heavy atom distances among the three fluoroethanols now seem consistent with expectations arising from bond variations from the electronegativities of the added fluorine atoms. Also the

Table 10 Structural parameters (Å and °) for *gauche* 2-fluoroethanol

Structural parameters	MP2(full)/6-311+G(d,p)	ED ^a r_g	MW ^b	Adjusted r_0 parameters ^c
r(C ₁ –C ₂)	1.508	1.518(6)	1.503	1.510(5)
r(C ₁ –O)	1.416	1.432(16)	1.411	1.418(5)
r(O–H)	0.962	0.955(36)	1.008	0.962(2)
r(C ₁ –H ₆)	1.093	1.091(18)	1.093	1.093(2)
r(C ₁ –H ₅)	1.092	1.091(18)	1.093	1.092(2)
r(C ₂ –H ₈)	1.093	1.091(18)	1.093	1.093(2)
r(C ₂ –H ₇)	1.097	1.091(18)	1.093	1.097(2)
r(C ₂ –F ₄)	1.399	1.398(24)	1.395	1.402(5)
∠(COH)	106.6	105.8	105.8	107.6(5)
∠(CCO)	111.8	112.3(14)	112.8	111.8(5)
∠(F ₄ CC)	108.5	108.5(8)	109.0	107.6(5)
τ(F ₄ CCO)	63.5	64.0(8)	62.2(10)	63.7(5)
τ(CCOH)	–57.0	–54.6(78)	–55.5(30)	–57.4(5)
A	15845.35	15860.17	15875.18	15876.05
B	5458.35	5401.22	5409.26	5409.24
C	4557.23	4521.35	4525.83	4526.72

^a Ref. [23]^b Ref. [24]; all the values are assumed parameters except the two dihedrals^c This study

effects of the internal hydrogen bond of the hydroxyl group to the fluorine atom are consistent across the molecules, which are indicated by the non-bonded H...F distance of 2.481, 2.496, and 2.512 Å for 2-fluoroethanol, 2,2-difluoroethanol, 2,2,2-trifluoroethanol, respectively. These values differ from the distances previously reported for the values given earlier from the independent microwave studies of each molecule.

Acknowledgment JRD acknowledges the University of Missouri–Kansas City for a Faculty Research Grant for partial financial support of this research.

References

- Sellevag SR, Nielsen CJ, Søvde OA, Myhre G, Sundet JK, Stordal F, Isaken SAI (2004) Atmos Environ 38:6725. doi:10.1016/j.atmosenv.2004.09.023
- Vaynberg J, Ng LM (2005) Surf Sci 577:175. doi:10.1016/j.susc.2004.12.031
- Perttilä M (1979) Spectrochim Acta A 35A:37. doi:10.1016/0584-8539(79)80062-8
- Marstokk KM, Møllendal H (1980) Acta Chem Scand A 34:765. doi:10.3891/acta.chem.scand.34a-0765
- Durig JR, Ganguly A, El Defrawy AM, Gounev TK, Guirgis GA (2008) Spectrochim Acta A 71A:1379. doi:10.1016/j.saa.2008.04.010
- Durig JR, Ganguly A, El Defrawy AM, Zheng C, Badawi HM, Herrebout WA, van Veken BJ, Guirgis GA, Gounev TK (2009) J Mol Struct. doi:10.1016/j.molstruc.2009.01.014
- Wei L, Ganguly A, Minei AJ, Lindeke GL, Pringle WC, Novick SE, Durig JR (2009) J Mol Struct. doi:10.1016/j.molstruc.2009.01.040
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, revision E.01. Gaussian, Inc., Wallingford, CT
- Pulay P (1969) Mol Phys 17:197. doi:10.1080/00268976900100941
- Møller C, Plesset MS (1934) Phys Rev 46:618. doi:10.1103/PhysRev.46.618
- Guirgis GA, Zhu X, Yu Z, Durig JR (2000) J Phys Chem A 104:4383. doi:10.1021/jp993430o
- Chantry GW (1971) The Raman effect, vol 2. Marcel Dekker Inc., New York, NY
- Frisch MJ, Yamaguchi Y, Gaw JF, Schaefer HFIII, Binkley JS (1986) J Chem Phys 84:531. doi:10.1063/1.450121
- Amos RD (1986) Chem Phys Lett 124:376. doi:10.1016/0009-2614(86)85037-0
- Polavarapu PL (1990) J Phys Chem 94:8106. doi:10.1021/j100384a024
- Durig JR, Ng KW, Zheng C, Shen S (2004) Struct Chem 15:149. doi:10.1023/B:STUC.0000011249.33964.2c
- McKean DC (1984) J Mol Struct 113:251. doi:10.1016/0022-2860(84)80149-0
- Van der Veken BJ, Herrebout WA, Durig DT, Zhao W, Durig JR (1999) J Phys Chem A 103:1976. doi:10.1021/jp9835162
- Perttilä M, Murto J, Kivinen A, Turunen K (1978) Spectrochim Acta A 34A:9. doi:10.1016/0584-8539(78)80178-0
- Xu L-H, Fraser GT, Lovas FJ, Suenram RD, Gillies CW, Warner HE, Gillies JZ (1995) J Chem Phys 103:9541. doi:10.1063/1.469968
- Beagley B, Jones MO, Zanjanchi MA (1979) J Mol Struct 56:215. doi:10.1016/0022-2860(79)80158-1
- Culot JP (1972) Fourth Austin symposium on gas phase molecular structure, Austin, Texas, Paper T8
- Huang J, Hedberg K (1989) J Am Chem Soc 111:6909. doi:10.1021/ja00200a003
- Buckton KS, Azrak RG (1970) J Chem Phys 52:5652. doi:10.1063/1.1672840
- Nygaard L (1966) Spectrochim Acta A 22:1261
- Azrak RG, Wilson EB (1970) J Chem Phys 52:5299. doi:10.1063/1.1672779