

Available online at www.sciencedirect.com



Spectrochimica Acta Part A 60 (2004) 829-841

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Infrared and Raman spectra, conformational stability, ab initio calculations and vibrational assignment of 2-fluorobutane

James R. Durig^{a,*}, Xiaodong Zhu^a, Gamil A. Guirgis^b

^a Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499, USA
^b Department of Chemistry & Biochemistry, College of Charleston, Charleston, SC 29403, USA

Received 27 May 2003; accepted 25 June 2003

Abstract

The infrared spectra $(3500-50 \text{ cm}^{-1})$ of gas and solid and the Raman spectrum $(3500-50 \text{ cm}^{-1})$ of liquid 2-fluorobutane, CH₃CHFCH₂CH₃, have been recorded. Variable temperature studies over the range -105 to $-150 \,^{\circ}\text{C}$ of the infrared spectra $(3500-400 \text{ cm}^{-1})$ of the sample dissolved in liquid krypton have also been recorded. By utilizing the relative intensities of six conformer pairs each for both Me-*trans*/F-*trans* and Me-*trans*/H-*trans*, the Me-*trans* conformer is found to be the lowest energy form with an enthalpy difference to the F-*trans* conformer of $102 \pm 10 \text{ cm}^{-1}$ ($1.21 \pm 0.12 \text{ kJ} \text{ mol}^{-1}$) whereas the H-*trans* conformer is the highest energy form with an enthalpy difference of $208 \pm 21 \text{ cm}^{-1}$ ($2.49 \pm 0.25 \text{ kJ} \text{ mol}^{-1}$) higher than the Me-*trans* form. At ambient temperature, it is estimated that there is $50 \pm 2\%$ of the Me-*trans* form, $31 \pm 1\%$ of the F-*trans* form, and $19 \pm 1\%$ of the H-*trans* conformer present. Equilibrium geometries and total energies of the three conformers have been determined by ab initio calculations with full electron correlation by the perturbation method to second order using a number of basis sets. A complete vibrational assignment is proposed for the Me-*trans* conformer and many of the fundamentals have been identified for the other two forms based on the force constants, relative infrared and Raman intensities, and depolarization ratios obtained from MP2/6-31G(d) ab initio calculations. The spectroscopic and theoretical results are compared to the corresponding properties for some similar molecules. © 2003 Elsevier B.V. All rights reserved.

Keywords: Conformational stabilities; FT-IR and Raman spectra; Ab initio calculations; Krypton solutions; 2-Fluorobutane

1. Introduction

The conformational stabilities, structural parameters, and vibrational spectra of the propyl derivatives (CH₃CH₂CHXY; X = H, CH₃; Y = H, F, Cl, Br, I, CN, C=CH, except propane) have been studied extensively [1–8]. For the 1-halopropanes [1,2], the experimental results indicate that the *gauche* conformer is the more stable form irrespective of the halogen substituents. The values of the enthalpy difference are 99, 52, and 72 cm⁻¹ for fluoride [1], chloride [2], and bromide [2], respectively, which are consistent with the ab initio predictions with the basis set (MP2/6-311+G(2d, 2p)). For X = CH₃, the compounds are 2-substitued butanes and three stable conformers are expected to be present in the fluid phases. It has been previously shown [4–6] that the Me-*trans* conformer where two methyl groups are *trans* to each other, is the lowest energy

1386-1425/\$ – see front matter 0 2003 Elsevier B.V. All rights reserved. doi:10.1016/S1386-1425(03)00308-1

form whereas the H-trans conformer with the hydrogen atom *trans* to the methyl group has the highest energy for several molecules. The electron diffraction studies for 2-chlorobutane [4] and 2-bromobutane [4] show that the Me-trans form is the lowest energy form for both molecules. Similar conformational stability results have been obtained for 2-methylbutyronitrile, CH3CH2CH2CH(CH3)CN, and 3-methyl-1-pentyne, $HC \equiv CCH(CH_3)CH_2CH_3$, and are found to be in agreement with the molecular mechanics MM2 predictions [6]. However, the ab initio calculations with smaller basis sets may predict the wrong conformational stability. For example, the MP2/6-31G(d)and MP2/6-311G(d) calculations for 1-chloropropane and 1-bromopropane predicted the trans conformer as the more stable form which are not consistent with the experimental results [2].

We recently investigated the conformational stability of 4-fluoro-1-pentyne (HC \equiv CCH₂CHFCH₃) [9] which exists in three stable conformers in the fluid states and the F-*trans* form was found lowest in energy. The determination of the second most stable conformer was a major challenge since

^{*} Corresponding author. Tel.: +1-816-235-6038;

fax: +1-816-235-2290.

E-mail address: durigj@umkc.edu (J.R. Durig).

calculations utilizing the full electron correlation method at the MP2 level predicted the H-*trans* conformer the next stable conformer. However, hybrid density functional theory (DFT) calculations using the B3LYP method predicted the Me-*trans* form more stable with several basis sets and the least stable form to be the H-*trans* conformer. Therefore, a temperature dependent infrared study is essential in determining the conformational stabilities. In particular, since the stability of the second conformer has been predicted poorly from theoretical calculations for many three-conformer molecules, an experimental investigation is necessary to eliminate the confusion from theoretical calculations.

In the previous study of 2-fluorobutane [5], the vibrational assignment was not complete, and the experimental enthalpy differences among the three conformers was not determined and neither the Raman nor the far infrared spectra were reported. Therefore, temperature dependent infrared spectra of the sample dissolved in liquid krypton have been recorded in this study in order to obtain a reliable value of the enthalpy differences among the three possible conformers. The infrared spectra of 2-fluorobutane in the gaseous and solid phases and the Raman spectrum of the liquid have been recorded for the purpose of providing a complete vibrational assignment for the most stable conformer. In order to facilitate the vibrational assignment, ab initio calculations utilizing the perturbation method to the second order (MP2) and hybrid DFT calculations by the B3LYP method have been carried out with various basis sets. The results of these vibrational spectroscopic and theoretical studies are reported herein.

2. Experimental

All chemicals used in the preparations were purchased from Aldrich Chem. Co., Milwaukee, WI. The 2-fluorobutane sample was prepared by the previously reported method with modification [10]. The 2-butyltosylate was prepared by adding pyridine dropwise to 2-butanol and *p*-toluenesulfonyl chloride mixture in an ice bath. The reaction was allowed to proceed for 2h and quenched by pouring the mixture into ice-cold water. The tosylate was extracted by ethyl ether and washed sequentially with cold water, diluted potassium hydroxide, and cold water. The ethyl ether was removed by vacuum evaporation. The 2-fluorobutane sample was obtained by using potassium fluoride to fluoronate the 2-butyltosylate. The 2-butyltosylate sample was mixed with 2-methoxyethyl ether and potassium fluoride while the system pressure was reduced to 13.3 Pa with continual stirring. The temperature was then raised to 70 °C and the reaction was initiated and lasted 3h. The sample of 2-fluorobutane was removed from the system every 5-10 min by using a liquid nitrogen trap. Further purification of the sample was performed using a low-temperature, low-pressure fractionating column. The sample was stored under vacuum at low temperature and the



Fig. 1. Mid-infrared spectra of 2-fluorobutane in: (A) gas; and (B) polycrystalline solid.

purity was checked by comparing the mid-infrared spectrum of the gas with the previously reported spectrum [5].

The mid-infrared spectra of the gas and solid (Fig. 1) were obtained using a Perkin–Elmer model 2000 Fourier transform spectrophotometer equipped with a nichrome wire source, a Ge/CsI beam splitter, and a DTGS detector. The spectrum of the gas was obtained with the sample contained in 10 cm cell fitted with CsI windows. The spectrum of the solid was obtained by condensing the sample on a CsI substrate held at \sim 77 K by boiling liquid nitrogen, housed in a vacuum cell fitted with CsI windows. The sample was repeatedly annealed until no further changes were observed in the spectrum. The theoretical resolution used to obtain the spectra of both the gas and the solid was 1.0 cm⁻¹.

The far infrared spectra of the gas and solid (Fig. 2) were recorded on the previously described Perkin–Elmer 2000 spectrometer. A grid beam splitter and a cryostat cell fitted with polyethylene windows was used to record the spectrum of the solid with the sample being deposited on a silicon substrate at 77 K and multiple annealings were performed in order to obtain a good polycrystalline solid. For the spectrum of the gas, the sample was contained in a 10 cm cell equipped with polyethylene windows. The spectra were recorded at a spectral resolution of 1.0 cm^{-1} . Typically, 128 scans were used for both the sample and reference data to give a satisfactory signal-to-noise ratio. The interferograms were averaged and then transformed with a boxcar truncation function.

The mid-infrared spectra of the sample dissolved in liquefied krypton (Fig. 3A) as a function of temperature were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr



Fig. 2. Far-infrared spectra of 2-fluorobutane in: (A) gas; and (B) polycrystalline solid.

beamsplitter, and a DTGS detector. The temperature studies ranged from -105 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. For each temperature investigated, 100 interferograms were recorded at a 1.0 cm^{-1} resolution, averaged, and transformed with a boxcar truncation function.



Fig. 3. Mid-infrared spectra of 2-fluorobutane in: (A) krypton solution at -125 °C; (B) simulated infrared spectrum of three conformer mixture with the ΔH of 102 and 208 cm⁻¹ for Me-*trans/F*-*trans* and Me-*trans/H*-*trans* conformer pairs, respectively; (C) calculated spectrum of the pure H-*trans* conformer; (D) calculated spectrum of the pure F-*trans* conformer; and (E) calculated spectrum of the pure Me-*trans* conformer.



Fig. 4. Raman spectra of 2-fluorobutane in: (A) liquid; (B) simulated infrared spectrum of the three conformer mixture with the ΔH of 102 and 208 cm⁻¹ for Me-*trans/F-trans* and Me-*trans/H-trans* conformer pairs at 25 °C; (C) calculated spectrum of the pure H-*trans* conformer; (D) calculated spectrum of the pure F-*trans* conformer; and (E) calculated spectrum of the pure Me-*trans* conformer.

The Raman spectrum (Fig. 4A) of the liquid was recorded on a SPEX model 1403 spectrophotometer equipped with a Spectra-Physics model 164 argon ion laser operating on the 514.5 nm line. The laser power used was 0.5 W with a spectral bandpass of 3 cm^{-1} . The spectra of the liquid and solid were recorded with the sample sealed in a Pyrex glass capillary. The wave numbers for all of the observed fundamental bands by the different techniques in the various physical states are listed in Tables 1–3 for Me-*trans*, F-*trans*, and H-*trans* conformers, respectively.

3. Ab initio calculation

The LCAO-MO-SCF ab initio calculations were performed with the Gaussian-98 program [11] using Gaussian type basis functions. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all of the geometric parameters using the gradient method of Pulay [12]. Calculated energies were determined at the MP2 level with full electron correlation with various basis sets up to 6-311+G(2d, 2p) as well as hybrid density functional theory calculations by B3LYP method and the results are listed in Table 4 (B3LYP results not listed). The structural parameters for the three stable conformers of 2-fluorobutane from RHF and MP2 calculations are listed in Table 4.

To determine the degree of mixing of symmetry coordinates and to obtain a more complete description of the

| Table 1 | |
|----------------------------------------------------------|------------------------------------------------|
| Observed and calculated wave numbers (cm ⁻¹) |) for the Me-trans conformer of 2-fluorobutane |

| Vibration nunber | Description ^a | Ab initio ^b | Fixed scaled ^c | IR intensities ^d | Raman activities ^e | Gas | Krypton | Solid ^f | Raman | PED ^g |
|-----------------------|--------------------------------------------|---------------------------|------------------------------|--------------------------------|----------------------------------|------|------------|--------------------|-------|--------------------------------------------------------------------------------------|
| <i>v</i> ₁ | *CH ₃ antisymmetric | 3220 | 3021 | 17.4 | 36.1 | 2997 | | | | 63S ₁ , 34S ₄ |
| ν_2 | CH ₃ antisymmetric | 3214 | 3015 | 17.3 | 60.2 | 2993 | 2982 | 2988 | 2983 | 92S ₂ |
| <i>v</i> ₃ | CH ₃ antisymmetric | 3208 | 3010 | 17.7 | 52.5 | 2984 | | 2979 | 2982 | 92S ₃ |
| ν_4 | *CH ₃ antisymmetric stretch | 3196 | 2998 | 28.0 | 56.9 | 2975 | 2971 | 2972 | | 65S ₄ , 32S ₁ |
| ν_5 | CH ₂ antisymmetric stretch | 3157 | 2961 | 15.6 | 47.6 | 2940 | 2943 | 2941 | 2940 | 94S ₅ |
| ν_6 | CH ₃ symmetric stretch | 3115 | 2922 | 11.4 | 117.8 | 2918 | 2925 | 2919 | 2915 | 97S ₆ |
| ν ₇ | *CH ₃ antisymmetric stretch | 3113 | 2920 | 23.9 | 92.3 | 2918 | 2912 | | 2915 | 96S ₇ |
| ν_8 | CH ₂ symmetric stretch | 3104 | 2912 | 28.6 | 21.6 | 2893 | 2886 | 2884 | 2888 | 64S ₈ , 31S ₉ |
| V9 | CH stretch | 3100 | 2908 | 13.8 | 106.0 | 2869 | 2862 | 2870 | 2877 | 66S ₉ , 32S ₉ |
| ν_{10} | *CH ₃ antisymmetric deformation | 1574 | 1494 | 7.5 | 11.4 | 1473 | 1468 | 1479 | | $75S_{10}, 12S_{12}$ |
| v_{11} | CH ₃ antisymmetric deformation | 1564 | 1484 | 9.8 | 4.1 | 1465 | | 1467 | | $54S_{11}, 23S_{12}$ |
| v_{12} | *CH ₃ antisymmetric deformation | 1563 | 1483 | 0.4 | 25.9 | | 1456 | 1462 | 1458 | $65S_{12}, 25S_{11}$ |
| v_{13} | CH ₃ antisymmetric deformation | 1551 | 1472 | 4.8 | 21.1 | 1449 | 1445 | 1450 | 1449 | $78S_{13}, 11S_{14}$ |
| v_{14} | CH ₂ deformation | 1540 | 1462 | 0.3 | 5.7 | 1441 | 1436 | 1438 | | 81S ₁₄ |
| v_{15} | CH bend (out-plane) | 1477 | 1403 | 9.9 | 3.6 | 1390 | 1384 | 1389 | 1387 | $18S_{15}, 28S_{17}, 15S_{19}, 14S_{16}$ |
| v_{16} | CH bend (in-plane) | 1470 | 1395 | 15.1 | 0.6 | 1384 | 1380 | 1383 | | $73S_{16}, 19S_{17}$ |
| v_{17} | *CH ₃ symmetric deformation | 1460 | 1386 | 8.3 | 4.8 | | 1373 | 1376 | 1375 | $38S_{17}, 17S_{19}, 28S_{19}, 16S_{15}$ |
| ν_{18} | CH ₃ symmetric deformation | 1431 | 1361 | 13.2 | 6.8 | 1353 | 1350 | 1350 | 1345 | 66S ₁₈ |
| v_{19} | CH ₂ wag | 1378 | 1309 | 2.0 | 3.2 | 1305 | 1303 | 1303 | 1304 | $39S_{19}, 37S_{15}$ |
| v_{20} | CH ₂ twist | 1339 | 1272 | 0.9 | 8.9 | 1271 | 1268 | 1268 | 1271 | $62S_{20}, 17S_{26}$ |
| v_{21} | CH ₃ rock | 1243 | 1187 | 6.1 | 1.8 | 1181 | 1174 | 1179 | 1175 | $19S_{21}, 15S_{28}, 12S_{29}, 12S_{34}, 11S_{26}$ |
| v_{22} | CH ₃ rock | 1200 | 1144 | 19.5 | 4.0 | 1137 | 1132 | 1126 | 1129 | $30S_{22}, 13S_{27}, 13S_{31}$ |
| ν_{23} | C_3C_4 stretch | 1185 | 1134 | 15.8 | 6.0 | 1125 | 1120 | 1115 | 1120 | $224S_{23}, 12S_{25}, 10S_{29}$ |
| v_{24} | C ₁ C ₂ stretcn | 1094 | 1039 | 14.7 | 2.4 | 1033 | 1032 | 1032 | 1031 | $535_{24}, 185_{23}, 135_{27}$ |
| V ₂₅ | *CH ₃ rock | 1042 | 989 | 14.4 | 5.0 | 98/ | 991 | 995 | 985 | $1/5_{25}, 155_{22}, 125_{19}$ |
| V26 | CE stratch | 055 | 905 | 0.0 | 0.3 5.2 | 908 | 907 800 | 900 | 9/1 | $115_{26}, 555_{21}, 175_{25}, 115_{15}$ |
| V27 | Cr succi CaCa stretch | 955 859 | 905 816 | 23.3 | 5.5 7 1 | 804 | 873 | 823 | 824 | $135_{27}, 515_{22}, 115_{24}$ $185_{22}, 175_{24}, 135_{22}, 135_{24}, 105_{22}$ |
| V28 | CH ₂ twist | 800 | 761 | 4.2 | 2.5 | 770 | 765 | 764 | 765 | $105_{28}, 175_{21}, 155_{23}, 155_{26}, 105_{29}$ |
| V29 | $C_1C_2C_2$ bend | 503 | /01 | 2.8 | 2.5 | /03 | /03 | /04 | 103 | $19S_{20}$, $25S_{20}$, $17S_{26}$, $14S_{20}$ |
| V30 | CCF bend | 470 | 459 | 33 | 0.4 | 457 | 457 | 459 | 458 | $49S_{21}$ $14S_{22}$ $13S_{20}$ |
| V31 | (out-nlane) | 470 | 457 | 5.5 | 0.4 | 437 | 157 | 457 | 450 | 49631, 14632, 15629 |
| 1/22 | CCF bend (in-nlane) | 373 | 370 | 3.6 | 0.5 | 369 | _ | 374 | 372 | 37822 27824 12821 |
| - 52 V22 | CH ₂ torsion | 253 | 253 | 0.2 | 0.03 | 507 | _ | 260 | 512 | 76S ₂₂ , 12S ₂₅ |
| - 55 V34 | $C_2C_3C_4$ bend | 246 | 245 | 0.5 | 0.02 | 255 | _ | 252 | | $25S_{34}, 37S_{30}, 15S_{22}$ |
| V35 | *CH ₃ torsion | 233 | 236 | 1.4 | 0.06 | 243 | _ | 237 | | 62S ₃₅ |
| v ₃₆ | Asymmetric torsion | 118 | 118 | 0.5 | 0.02 | 108 | - | 142 | | 90S ₃₆ |

 $^{a}% \left(A_{1}^{a}\right) =0$ Asterisk indicates the $C_{1}% \left(A_{1}^{a}\right) =0$ atom.

^b Calculated with the MP2/6-31G(d) basis set.

^c Scaled MP2/6-31G(d) calculations with factors of 0.88 were used for the CH stretches, 0.9 for the heavy atom stretches and CH bends, and 1.0 for all other modes.

 d Calculated infrared intensities in kilometer per mole with the MP2/6-31G(d) basis set. e Calculated Raman activities in Å 4 amu $^{-1}$ with the MP2/6-31G(d) basis set.

^f Observed solid frequencies are from the infrared spectrum.

g Calculated with the MP2/6-31G(d) basis set; contributions less than 10% are omitted.

Table 2 Observed and calculated wave numbers (cm^{-1}) for the F-*trans* conformer of 2-fluorobutane

| Vibration nunber | Description ^a | Ab initio ^b | Fixed scaled ^c | IR intensities ^d | Raman activities ^e | Gas | Krypton | Raman | PED^{f} |
|-----------------------|--------------------------------------------|---------------------------|------------------------------|--------------------------------|----------------------------------|------|---------|-------|-----------------------------------------------------------|
| v ₁ | *CH ₃ antisymmetric stretch | 3196 | 2998 | 28.7 | 43.7 | | | | $55S_1, 38S_4$ |
| ν_2 | CH ₃ antisymmetric stretch | 3211 | 3012 | 19.8 | 38.0 | | | | 77S ₂ , 17S ₃ |
| <i>v</i> ₃ | CH ₃ antisymmetric stretch | 3216 | 3017 | 13.5 | 66.4 | | | | $73S_3, 21S_2$ |
| ν_4 | *CH ₃ antisymmetric stretch | 3205 | 3006 | 29.0 | 33.2 | 2989 | | | $55S_4, 30S_1, 11S_4$ |
| <i>v</i> ₅ | CH ₂ antisymmetric stretch | 3165 | 2969 | 10.8 | 76.2 | 2952 | | | 90S ₅ |
| ν_6 | CH ₃ symmetric stretch | 3116 | 2924 | 6.3 | 122.9 | | | | 97S ₆ |
| v_7 | *CH ₃ antisymmetric stretch | 3109 | 2916 | 8.3 | 106.7 | | | | 82S ₇ , 14S ₇ |
| ν_8 | CH ₂ symmetric stretch | 3113 | 2920 | 33.1 | 18.4 | | | | 81S ₈ , 14S ₇ |
| <i>V</i> 9 | CH stretch | 3100 | 2908 | 24.9 | 94.1 | | | | 92S ₉ |
| v_{10} | *CH ₃ antisymmetric deformation | 1574 | 1495 | 7.0 | 4.6 | 1478 | | | $38S_{10}, 38S_{11}, 12S_{14}$ |
| v_{11} | CH ₃ antisymmetric deformation | 1571 | 1491 | 5.2 | 14.9 | 1469 | | | $29S_{11}, 31S_{14}, 20S_{12}$ |
| v_{12} | *CH ₃ antisymmetric deformation | 1565 | 1485 | 7.4 | 5.3 | 1463 | 1465 | | $32S_{12}, 35S_{10}, 18S_{11}$ |
| v ₁₃ | CH ₃ antisymmetric deformation | 1552 | 1473 | 4.9 | 19.1 | | | | 78S ₁₃ |
| v_{14} | CH ₂ deformation | 1550 | 1470 | 0.2 | 24.4 | | | | $47S_{14}, 35S_{12}, 11S_{10}$ |
| v_{15} | CH bend (out-plane) | 1477 | 1403 | 20.2 | 3.1 | | | | $15S_{15}, 40S_{17}, 21S_{16}$ |
| v_{16} | CH bend (in-plane) | 1475 | 1399 | 10.9 | 2.9 | | | | 71S ₁₆ |
| v ₁₇ | *CH ₃ symmetric deformation | 1432 | 1361 | 6.9 | 3.3 | | 1344 | | $27S_{17}, 32S_{18}, 20S_{15}$ |
| v_{18} | CH ₃ symmetric deformation | 1455 | 1382 | 12.7 | 5.9 | 1370 | | | $17S_{18}, 25S_{15}, 23S_{19}$ |
| V19 | CH ₂ wag | 1373 | 1304 | 2.3 | 5.6 | | | | $39S_{19}, 36S_{18}$ |
| v_{20} | CH ₂ twist | 1329 | 1263 | 1.6 | 5.6 | 1264 | | | $60S_{20}, 16S_{26}$ |
| v_{21} | CH ₃ rock | 1245 | 1187 | 5.6 | 0.8 | 1176 | | | $19S_{21}, 27S_{29}, 21S_{26}, 13S_{34}$ |
| v_{22} | CH ₃ rock | 1176 | 1125 | 40.9 | 4.3 | 1112 | 1106 | 1103 | $29S_{22}, 24S_{27}, 13S_{31}, 12S_{25}$ |
| v_{23} | C ₃ C ₄ stretch | 1216 | 1161 | 5.2 | 5.4 | | 1151 | | $23S_{23}, 20S_{28}, 13S_{15}$ |
| v_{24} | C ₁ C ₂ stretch | 1098 | 1043 | 10.2 | 3.2 | | | | $58S_{24}, 13S_{25}, 11S_{27}$ |
| v_{25} | *CH ₃ rock | 1039 | 985 | 19.5 | 6.5 | | | | $13S_{25}, 18S_{23}, 18S_{27}$ |
| v_{26} | *CH ₃ rock | 1004 | 952 | 5.2 | 1.4 | 963 | | | $13S_{26}, 40S_{21}, 12S_{20}, 11S_{15}$ |
| v_{27} | CF stretch | 958 | 909 | 17.4 | 4.3 | 909 | 905 | 898 | $28S_{27}, 31S_{22}, 13S_{25}$ |
| ν_{28} | C_2C_3 stretch | 862 | 819 | 2.9 | 5.8 | 829 | 826 | | $19S_{28}, 16S_{23}, 14S_{21}, 11S_{25}, 10S_{26}$ |
| V29 | CH ₂ twist | 812 | 771 | 3.5 | 1.8 | | 780 | 782 | 47S ₂₉ , 22S ₂₆ , 13S ₂₃ |
| v_{30} | $C_1C_2C_3$ bend | 439 | 432 | 3.0 | 0.9 | 433 | 436 | 439 | $22S_{30}, 32S_{34}, 19S_{32}$ |
| v ₃₁ | CCF bend (out-plane) | 497 | 482 | 5.1 | 1.5 | 488 | 490 | | 51S ₃₁ |
| V32 | CCF bend (in-plane) | 397 | 394 | 4.2 | 0.5 | 398 | | | 59S ₃₂ , 22S ₃₄ |
| V33 | CH ₃ torsion | 273 | 272 | 0.6 | 0.05 | 287 | | | 47S ₃₃ , 27S ₃₅ |
| v_{34} | $C_2C_3C_4$ bend | 259 | 257 | 1.4 | 0.1 | | | | $13S_{34}, 42S_{30}, 25S_{31}, 12S_{33}$ |
| V35 | *CH ₃ torsion | 226 | 226 | 0.2 | 0.01 | | | | 59S ₃₅ , 32S ₃₃ |
| v_{36} | Asymmetric torsion | 107 | 107 | 0.62 | 0.04 | | | | 90S ₃₆ |

^a Asterisk indicates the C₁ atom.

^b Calculated with the MP2/6-31G(d) basis set.

^c Scaled MP2/6-31G(d) calculations with factors of 0.88 were used for the CH stretches, 0.9 for the heavy atom stretches and CH bends, and 1.0 for all other modes.

^d Calculated infrared intensities in kilometer per mole with the MP2/6-31G(d) basis set.

 e Calculated Raman activities in ${\rm \AA}^{4}\,amu^{-1}$ with the MP2/6-31G(d) basis set.

 $^{\rm f}$ Calculated with the MP2/6-31G(d) basis set; contributions less than 10% are omitted.

molecular motions involved in the fundamental vibrations of 2-fluorobutane, a normal coordinate analysis has been carried out. The internal coordinates defined in Table 4 and shown in Fig. 5 were used to build the symmetry coordinates listed in Table 5. The B-matrix elements were used to convert the ab initio calculated force field from Cartesian coordinates into the force field in internal coordinates [13]. These force constants were used in a mass-weighted Cartesian coordinate calculation to reproduce the ab initio predicted frequencies and to determine the potential energy distributions (PED), which are given in Tables 1–3 for the three conformers. The diagonal elements of the force field in the internal coordinates were then modified with scaling



Fig. 5. Internal coordinates for 2-fluorobutane.

| Table 3 |
|------------------------------------------------------------------------------------------------------|
| Observed and calculated wave numbers (cm ⁻¹) for the H-trans conformer of 2-fluorobutane |

| Vibration nunber | Description ^a | Ab initio ^b | Fixed scaled ^c | IR intensities ^d | Raman activities ^e | Gas | Krypton | Raman | PED ^f |
|-----------------------|--------------------------------------------|---------------------------|------------------------------|--------------------------------|----------------------------------|------|---------|-------|---------------------------------------------------------|
| v_1 | *CH ₃ antisymmetric stretch | 3217 | 3018 | 17.1 | 36.3 | | | | 75S1, 16S ₄ |
| v_2 | CH ₃ antisymmetric stretch | 3224 | 3024 | 16.2 | 41.6 | | | | $78S_2, 12S_3$ |
| <i>v</i> ₃ | CH ₃ antisymmetric stretch | 3209 | 3010 | 16.8 | 52.7 | | | | 85S ₃ ,14S ₂ |
| v_4 | *CH ₃ antisymmetric stretch | 3202 | 3004 | 27.5 | 52.6 | | | | $82S_4, 13S_1$ |
| ν_5 | CH ₂ antisymmetric stretch | 3158 | 2962 | 14.4 | 74.1 | | | | 96S ₅ |
| v_6 | CH ₃ symmetric stretch | 3121 | 2927 | 4.2 | 237.1 | | | | 59S ₆ , 31S ₇ |
| v_7 | *CH ₃ antisymmetric stretch | 3117 | 2924 | 22.2 | 6.8 | | | | 69S ₇ , 26S ₇ |
| ν_8 | CH ₂ symmetric stretch | 3101 | 2909 | 8.4 | 51.1 | | | | 59S ₈ , 40S ₉ |
| <i>v</i> 9 | CH stretch | 3113 | 2921 | 50.4 | 57.9 | 2897 | | | 51S ₉ , 33S ₈ , 13S ₁₆ |
| v_{10} | *CH ₃ antisymmetric deformation | 1578 | 1497 | 2.9 | 4.6 | | | | $42S_{10}, 27S_{12}, 20S_{11}$ |
| v_{11} | CH ₃ antisymmetric deformation | 1573 | 1493 | 7.6 | 17.4 | | | | $38S_{11}, 43S_{10}$ |
| v_{12} | *CH ₃ antisymmetric deformation | 1562 | 1482 | 9.7 | 7.0 | 1463 | 1456 | | $50S_{12}, 28S_{11}, 10S_{14}$ |
| v_{13} | CH ₃ antisymmetric deformation | 1551 | 1473 | 2.0 | 18.9 | | | | $64S_{13}, 19S_{14}$ |
| v_{14} | CH ₂ deformation | 1542 | 1464 | 1.6 | 20.1 | | | | $67S_{14}, 21S_{13}$ |
| v_{15} | CH bend (out-plane) | 1481 | 1406 | 21.2 | 3.3 | | 1392 | | $21S_{15}, 35S_{17}, 18S_{16}$ |
| v_{16} | CH bend (in-plane) | 1474 | 1399 | 13.4 | 2.6 | | | | $57S_{16}, 24S_{17}$ |
| v_{17} | *CH ₃ symmetric deformation | 1438 | 1366 | 3.0 | 1.1 | | | | $31S_{17}, 27S_{15}, 21S_{18}$ |
| v_{18} | CH ₃ symmetric deformation | 1419 | 1351 | 16.1 | 4.3 | 1348 | 1344 | | $32S_{18}, 17S_{19}, 14S_{28}, 10S_{15}$ |
| v_{19} | CH ₂ wag | 1432 | 1359 | 1.8 | 1.7 | | | | $42S_{19}, 22S_{16}, 16S_{18}$ |
| v_{20} | CH ₂ twist | 1343 | 1275 | 0.2 | 14.5 | | | | $60S_{20}, 16S_{26}$ |
| v_{21} | CH ₃ rock | 1032 | 978 | 1.2 | 4.9 | | | | $33S_{21}, 40S_{24}$ |
| v_{22} | CH ₃ rock | 1205 | 1148 | 26.9 | 4.0 | 1157 | | | $23S_{22}, 17S_{27}, 11S_{18}$ |
| v_{23} | C ₃ C ₄ stretch | 1226 | 1170 | 4.2 | 1.7 | | | | $19S_{23}, 15S_{29}, 14S_{21}, 13S_{26}$ |
| v_{24} | C ₁ C ₂ stretch | 1177 | 1125 | 11.7 | 1.9 | | | | $16S_{24}, 21S_{25}, 11S_{21}$ |
| v_{25} | *CH ₃ rock | 1050 | 998 | 8.6 | 3.5 | 993 | | 995 | $35S_{25}, 17S_{19}, 11S_{22}$ |
| v_{26} | *CH ₃ rock | 1042 | 988 | 30.2 | 4.7 | 984 | 985 | | $16S_{26}, 26S_{27}, 23S_{23}, 18S_{20}$ |
| v_{27} | CF stretch | 948 | 900 | 20.4 | 6.1 | 898 | 894 | 898 | $31S_{27}, 27S_{22}, 14S_{24}, 10S_{25}$ |
| v_{28} | C ₂ C ₃ stretch | 831 | 790 | 3.1 | 7.6 | 787 | 794 | 795 | $29S_{28}, 22S_{23}, 10S_{29}$ |
| ν_{29} | CH ₂ twist | 806 | 766 | 0.7 | 1.8 | | | | $45S_{29}, 25S_{26}, 10S_{28}$ |
| v_{30} | $C_1C_2C_3$ bend | 607 | 589 | 2.0 | 0.3 | 591 | 588 | | $22S_{30}, 23S_{31}, 16S_{34}, 10S_{21}$ |
| v_{31} | CCF bend (out-plane) | 370 | 368 | 1.6 | 0.1 | | | | $39S_{31}, 31S_{34}$ |
| v_{32} | CCF bend (in-plane) | 421 | 417 | 5.9 | 0.6 | 420 | 418 | 422 | 73S ₃₂ |
| v33 | CH ₃ torsion | 257 | 255 | 1.6 | 0.2 | | | | $43S_{33}, 28S_{30}$ |
| v ₃₄ | $C_2C_3C_4$ bend | 294 | 292 | 0.1 | 0.1 | | | | $23S_{34}, 23S_{30}, 22S_{33}, 21S_{35}$ |
| v_{35} | *CH ₃ torsion | 221 | 221 | 0.6 | 0.04 | | | | $55S_{35}, 28S_{33}$ |
| v_{36} | Asymmetric torsion | 108 | 108 | 0.9 | 0.1 | | | | 88S ₃₆ |

^a Asterisk indicates the C₁ atom.

^b Calculated with the MP2/6-31G(d) basis set.

^c Scaled MP2/6-31G(d) calculations with factors of 0.88 were used for the CH stretches, 0.9 for the heavy atom stretches and CH bends, and 1.0 for all other modes.

^d Calculated infrared intensities in kilometer per mole with the MP2/6-31G(d) basis set.

 e Calculated Raman activities in ${\rm \AA}^{4}\,{\rm amu}^{-1}$ with the MP2/6-31G(d) basis set.

f Calculated with the MP2/6-31G(d) basis set; contributions less than 10% are omitted.

factors of 0.88 for the carbon-hydrogen stretches, 0.9 for the heavy atom stretches and carbon-hydrogen bends, and 1.0 for the methyl torsion and skeletal bends. The off-diagonal elements were scaled with the geometric averages of the scaling factors involved. The calculations were repeated to obtain the fixed scaled force fields and scaled vibrational frequencies.

The Raman (Fig. 4) and infrared (Fig. 3) spectra for 2-fluorobutane were predicted using "fixed scaled" frequencies; Raman scattering activities and infrared intensities determined from the Gaussian-98 program [11] from the MP2/6-31G(d) calculations. The Raman scattering cross sections, $\partial \sigma_j / \partial \Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activi-

ties and the predicted frequencies for each normal mode [14–17]. To obtain the polarized Raman cross sections, the polarizabilities are incorporated into S_j by multiplying it by $(1 - \rho_j)/(1 + \rho_j)$, where ρ_j is the depolarization ratio of the *j*th normal mode. The Raman scattering cross sections and the predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra.

Infrared intensities were calculated based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were taken from the ab initio calculations and transformed to normal coordinates by

$$\frac{\partial \mu_u}{\partial Q_i} = \sum_j \left(\frac{\partial \mu_u}{\partial X_j}\right) L_{ij}$$

| Table 4 | | | | | | | | |
|------------------------------------|-----------------------|----------------|-----------|-------------|------------|------------|------|--------------|
| Structural parameters ^a | of 2-fluorobutane for | r the F-trans, | Me-trans, | and H-trans | conformers | from ab in | itio | calculations |

| Parameter Syb ^b | | RHF/6-31G(d) | | | MP2/6-31G(d) | | | MP2/6-311+G(d, p) | | | MP2/6-311+G(2d, 2p) | | |
|---------------------------------|------------------|--------------|----------|----------|--------------|----------|----------|-------------------|----------|----------|---------------------|----------|----------|
| | | Me-trans | F-trans | H-trans | Me-trans | F-trans | H-trans | Me-trans | F-trans | H-trans | Me-trans | F-trans | H-trans |
| $r(C_1-C_2)$ | $\overline{R_1}$ | 1.528 | 1.529 | 1.529 | 1.524 | 1.525 | 1.524 | 1.526 | 1.523 | 1.527 | 1.522 | 1.524 | 1.523 |
| $r(C_2-C_3)$ | R_2 | 1.519 | 1.521 | 1.523 | 1.514 | 1.516 | 1.518 | 1.515 | 1.517 | 1.519 | 1.510 | 1.511 | 1.514 |
| $r(C_3-C_4)$ | R_3 | 1.516 | 1.516 | 1.517 | 1.511 | 1.512 | 1.512 | 1.512 | 1.513 | 1.513 | 1.507 | 1.508 | 1.508 |
| $r(C_3 - F_8)$ | R_4 | 1.383 | 1.382 | 1.383 | 1.410 | 1.409 | 1.410 | 1.407 | 1.406 | 1.407 | 1.410 | 1.409 | 1.410 |
| $r(C_1-H_5)$ | r_1 | 1.085 | 1.085 | 1.085 | 1.093 | 1.093 | 1.093 | 1.093 | 1.093 | 1.093 | 1.085 | 1.085 | 1.085 |
| $r(C_1 - H_6)$ | r_2 | 1.083 | 1.087 | 1.085 | 1.091 | 1.094 | 1.093 | 1.092 | 1.095 | 1.093 | 1.085 | 1.088 | 1.086 |
| $r(C_1-H_7)$ | r_3 | 1.087 | 1.085 | 1.084 | 1.094 | 1.093 | 1.092 | 1.094 | 1.093 | 1.093 | 1.087 | 1.086 | 1.085 |
| $r(C_2 - H_{10})$ | r5 | 1.087 | 1.086 | 1.087 | 1.096 | 1.095 | 1.097 | 1.096 | 1.095 | 1.097 | 1.089 | 1.087 | 1.089 |
| $r(C_2 - H_{11})$ | r_6 | 1.087 | 1.087 | 1.086 | 1.096 | 1.096 | 1.095 | 1.096 | 1.096 | 1.095 | 1.089 | 1.088 | 1.088 |
| $r(C_3-H_9)$ | r_4 | 1.085 | 1.085 | 1.084 | 1.098 | 1.098 | 1.097 | 1.407 | 1.096 | 1.407 | 1.089 | 1.089 | 1.088 |
| $r(C_4 - H_{12})$ | r_7 | 1.085 | 1.085 | 1.083 | 1.093 | 1.093 | 1.091 | 1.093 | 1.094 | 1.092 | 1.086 | 1.086 | 1.084 |
| $r(C_4 - H_{13})$ | r_8 | 1.085 | 1.084 | 1.085 | 1.093 | 1.092 | 1.094 | 1.094 | 1.093 | 1.094 | 1.086 | 1.086 | 1.087 |
| $r(C_4 - H_{14})$ | r_{9} | 1.084 | 1.084 | 1.084 | 1.092 | 1.092 | 1.092 | 1.092 | 1.092 | 1.092 | 1.086 | 1.085 | 1.085 |
| $\angle C_1 C_2 C_3$ | ϕ | 113.0 | 114.0 | 114.7 | 112.6 | 113.5 | 113.8 | 112.9 | 112.9 | 114.2 | 112.8 | 112.7 | 114.1 |
| $\angle C_2 C_3 C_4$ | Ψ | 114.0 | 115.2 | 115.7 | 114.2 | 114.9 | 115.4 | 113.9 | 114.6 | 115.1 | 113.9 | 114.6 | 115.2 |
| $\angle C_2 C_1 H_5$ | α_1 | 110.8 | 110.4 | 110.3 | 111.1 | 110.6 | 110.6 | 110.9 | 110.6 | 110.3 | 111.2 | 110.8 | 110.6 |
| $\angle C_2 C_1 H_6$ | α2 | 110.8 | 111.4 | 112.0 | 110.2 | 111.1 | 111.9 | 110.6 | 110.9 | 111.7 | 110.6 | 111.0 | 111.7 |
| $\angle C_2 C_1 H_7$ | α ₃ | 111.2 | 112.0 | 110.7 | 110.9 | 111.7 | 110.1 | 110.7 | 111.7 | 110.6 | 110.8 | 111.7 | 110.6 |
| $\langle C_2 C_2 H_2$ | Γ_1 | 108.3 | 107.3 | 108.3 | 107.8 | 107.3 | 107.8 | 108.2 | 107.7 | 108.2 | 108.1 | 107.7 | 108.1 |
| $/C_2C_2H_0$ | σ | 110.0 | 109.9 | 108.9 | 110.0 | 110.0 | 109.5 | 109.9 | 109.9 | 109.3 | 110.1 | 110.0 | 109.5 |
| $C_3C_2C_{10}$ | ¥1 | 108.4 | 107.3 | 108.3 | 107.9 | 107.5 | 108.4 | 108.0 | 107.7 | 107.8 | 108.0 | 107.8 | 107.8 |
| $\angle C_3C_2H_{11}$ | V2 | 108.3 | 108.6 | 107.4 | 108.4 | 108.1 | 107.4 | 107.7 | 108.3 | 107.5 | 107.9 | 108.3 | 107.6 |
| $/C_{2}C_{4}H_{12}$ | φ1 | 110.5 | 110.5 | 111.1 | 109.8 | 109.8 | 110.6 | 110.0 | 110.1 | 110.7 | 110.0 | 110.0 | 110.6 |
| $C_2C_4C_{12}$ | φ | 110.7 | 111.3 | 110.6 | 110.7 | 111.3 | 110.6 | 110.1 | 110.6 | 110.0 | 110.2 | 110.7 | 110.2 |
| $/C_{2}C_{4}H_{14}$ | φ ₂ | 110.2 | 109.8 | 109.9 | 110.3 | 109.8 | 109.9 | 110.4 | 110.0 | 110.1 | 110.6 | 110.2 | 110.2 |
| $\tau C_1 C_2 C_2 C_4$ | τ ₂ | 179.1 | -67.0 | 60.9 | 177.8 | -65.7 | 59.3 | 180.4 | -64.5 | 56.2 | 180.7 | -65.9 | 56.5 |
| $\tau C_2 C_2 C_1 H_5$ | τ. | 180.4 | 184.8 | 174.2 | 180.9 | 185.0 | 172.6 | 179.8 | 186.4 | 173.1 | 180.3 | 185.1 | 174.0 |
| THeC1C2H5 | •1 | 120.1 | 119.4 | 119.6 | 120.3 | 119.5 | 119.9 | 120.2 | 119.5 | 119.7 | 120.3 | 119.6 | 119.7 |
| $\tau H_7 C_1 C_2 H_5$ | | -119.8 | -119.7 | -119.5 | -120.1 | -119.8 | -119.5 | -119.9 | -119.9 | -119.5 | -120.0 | -120.0 | -119.6 |
| $\tau F_8 C_3 C_2 C_4$ | | -120.0 | -119.6 | -121.1 | -119.5 | -119.2 | -120.2 | -120.1 | -119.9 | -120.7 | -119.7 | -119.7 | -120.4 |
| $\tau H_0 C_2 C_2 C_4$ | | 124.3 | 125.0 | 124.9 | 125.0 | 125.3 | 124.4 | 124.8 | 125.0 | 124.0 | 125.2 | 125.2 | 124.4 |
| $\tau H_{10}C_2C_2C_1$ | | -122.1 | -121.6 | -123.6 | -121.9 | -122.0 | -123.6 | -122.5 | -121.6 | -123.1 | -122.5 | -121.6 | -123.1 |
| $\tau H_{11}C_2C_3C_1$ | | 122.2 | 123.4 | 121.5 | 122.6 | 123.0 | 121.4 | 122.0 | 122.8 | 122.1 | 122.1 | 122.8 | 122.1 |
| $\tau H_{12}C_4C_3C_2$ | τ2 | -57.5 | -55.1 | -61.6 | -57.2 | -55.2 | -61.0 | -56.9 | -54.2 | -62.6 | -56.8 | -54.9 | -61.7 |
| $\tau H_{12}C_4C_3C_{12}$ | - 2 | 120.3 | 120.8 | 120.8 | 120.1 | 120.6 | 120.6 | 119.9 | 120.4 | 120.3 | 119.8 | 120.3 | 120.3 |
| $\tau H_{14}C_4C_3C_{12}$ | | -119.7 | -119.4 | -119.5 | -119.6 | -119.3 | -119.4 | -120.1 | -119.9 | -120.0 | -120.1 | -119.9 | -119.9 |
| A | | 8363 | 7821 | 6575 | 8228 | 7798 | 6467 | 8179 | 7794 | 6455 | 8204 | 7837 | 6481 |
| В | | 3468 | 3437 | 3866 | 3496 | 3438 | 3914 | 3475 | 3449 | 3900 | 3498 | 3462 | 3926 |
| C | | 2701 | 2632 | 3199 | 2708 | 2631 | 3227 | 2693 | 2636 | 3203 | 2708 | 2649 | 3227 |
| $ \mu_{n} $ | | 0.078 | 1.593 | 0.480 | 0.051 | 1.727 | 0.531 | .137 | 1.984 | 0.742 | 0.137 | 1.928 | 0.704 |
| | | 1.786 | 1.072 | 1.537 | 1.898 | 1.108 | 1.633 | -2.154 | 1.231 | 1.803 | 2.089 | 1.204 | 1.760 |
| $ \mu_{\alpha} $ | | 0.497 | 0.331 | 0.918 | 0.517 | 0.356 | 0.963 | .583 | .401 | 1.115 | 0.563 | 0.374 | 1.073 |
| <i>µ</i> _+ | | 1.8555 | 1.9483 | 1.8538 | 1.9677 | 2.0821 | 1.9687 | 2.2359 | 2.3692 | 2.2460 | 2.1674 | 2.3034 | 2.1777 |
| $-(E + 256)^{\circ}$ | | 0.154133 | 0.152766 | 0.152534 | 0.870485 | 0.869100 | 0.869241 | 1.141151 | 1.140486 | 1,140203 | 1.215706 | 1.214995 | 1.214731 |
| $\Delta E \ (\mathrm{cm}^{-1})$ | | | 300 | 351 | | 304 | 273 | | 146 | 208 | | 156 | 214 |

^a Bond distances in angstrom (Å), angles in degrees, rotational constants in megahertz (MHz), and dipole moments in Debye.
^b Symbols for internal coordinates.
^c Energy in hartree.

Table 5 Symmetry coordinates for vibrations of 2-fluorobutane

| Description ^a | Symmetry coordinate |
|----------------------------------------|-------------------------------------------------------------------------------------|
| *CH ₃ antisymmetric stretch | $S_1 = r_2 - r_3$ |
| CH ₃ antisymmetric stretch | $S_2 = r_{57} - r_9$ |
| CH ₃ antisymmetric stretch | $S_3 = 2r_8 - r_7 - r_9$ |
| *CH ₃ antisymmetric stretch | $S_4 = 2r_1 - r_2 - r_3$ |
| CH ₂ symmetric stretch | $S_5 = r_5 - r_6$ |
| CH ₃ symmetric stretch | $S_6 = r_7 + r_8 + r_9$ |
| *CH ₃ symmetric stretch | $S_7 = r_1 + r_2 + r_3$ |
| CH ₂ symmetric stretch | $S_8 = r_5 + r_6$ |
| CH stretch | $S_9 = r_4$ |
| *CH ₃ antisymmetric | $S_{10}=2\zeta_2-\zeta_1-\zeta_3$ |
| deformation | |
| CH ₃ antisymmetric | $S_{11} = 2\varepsilon_3 - \varepsilon_1 - \varepsilon_2$ |
| deformation | |
| *CH ₃ antisymmetric | $S_{12} = \zeta_1 - \zeta_3$ |
| deformation | |
| CH ₃ antisymmetric | $S_{13} = \varepsilon_1 - \varepsilon_2$ |
| deformation | |
| CH ₂ symmetric deformation | $S_{14} = 4\delta - \beta_1 - \beta_2 - \gamma_1 - \gamma_2$ |
| CH bend (out-of-plane) | $S_{15} = 2\Delta - \eta - \sigma$ |
| CH bend (in-plane) | $S_{16} = \sigma - \eta$ |
| *CH ₃ symmetric deformation | $S_{17} = \zeta_1 + \zeta_2 + \zeta_3 - \alpha_1 - \alpha_2 - \alpha_3$ |
| CH ₃ symmetric deformation | $S_{18} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 - \phi_1 - \phi_2 - \phi_3$ |
| CH ₂ wag | $S_{19} = \beta_1 + \beta_2 - \gamma_1 - \gamma_2$ |
| CH ₂ twist | $S_{20} = \beta_2 - \beta_1 + \gamma_1 - \gamma_2$ |
| CH ₃ rock | $S_{21}=\phi_3-\phi_1$ |
| CH ₂ rock | $S_{22} = 2\phi_2 - \phi_1 - \phi_3$ |
| C ₃ C ₄ stretch | $S_{23} = R_3$ |
| C ₁ C ₂ stretch | $S_{24} = R_1$ |
| *CH ₃ rock | $S_{25} = 2\alpha_1 - \alpha_2 - \alpha_3$ |
| *CH ₃ rock | $S_{26} = \alpha_2 - \alpha_3$ |
| CF stretch | $S_{27} = R_4$ |
| C_2C_3 stretch | $S_{28} = R_2$ |
| CH ₂ twist | $S_{29} = \beta_2 - \beta_1 - \gamma_1 + \gamma_2$ |
| $C_1C_2C_3$ bend | $S_{30} = \Phi$ |
| CCF bend (out-of-plane) | $S_{31} = \Gamma_1 + \Gamma_2$ |
| CCF bend (in-plane) | $S_{32} = \Gamma_1 - \Gamma_2$ |
| CH ₃ torsion | $S_{33} = \tau_2$ |
| $C_2C_3C_4$ bend | $S_{34} = \psi$ |
| *CH ₃ torsion | $S_{35} = \tau_1$ |
| Asymmetric torsion | $S_{36} = \tau_2$ |

^a Asterisk indicates the C₁ atom.

where the Q_i is the *i*th normal coordinate, X_j is the *j*th Cartesian displacement coordinate, and L_{ii} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The experimental Raman spectrum of the liquid and mid-infrared spectrum of the krypton solution for 2-fluorobutane are included with the calculated spectra in Figs. 3A and 4A, respectively, for comparative purposes. The calculated spectrum of the mixture of the three conformers was obtained using the enthalpy differences obtained from the temperature study of the liquid krypton solution (Tables 6 and 7). The agreement between the calculated spectrum of the mixture of conformers and the experimental Raman spectrum of the liquid is reasonably good where the frequencies and their relative intensities of many of the lines are similar to those predicted by the ab initio calculations. The agreement between the calculated and experimental infrared spectra is also satisfactory. Therefore, these calculated spectra are useful for analytical purposes and contribute significantly to spectral interpretation and vibrational assignments, particularly to distinguishing bands due to the individual conformers.

4. Vibrational assignment

Although the vibrational spectrum of 2-florobutane has been reported previously [5], the data were not complete and the conformational stabilities were not determined. The vibrational assignments in the present study are based on the scaled ab initio MP2/6-31G(d) frequencies, infrared intensities, Raman activities, as well as characteristic "group frequencies" from similar molecules.

Several bands which were observed in the spectra of the fluid states were absent in the spectrum of the annealed polycrystalline solid. For example, the band at 588 cm^{-1} in the krypton solution disappeared in the solid state. This band is assigned to the fundamental of the H-*trans* conformer, since the nearest bands for the other two conformers are over 100 cm^{-1} apart, according to the ab initio MP2/6-31G(d)

| Temperature and intensity ratios from the conformational study of the Me-trans and F-trans conformers in | krypton solutio |)ľ |
|----------------------------------------------------------------------------------------------------------|-----------------|----|
|----------------------------------------------------------------------------------------------------------|-----------------|----|

| T (°C) | 1000/T (K) | I ₄₉₃ /I ₄₈₉ | I ₄₅₇ /I ₇₈₀ | I ₄₅₇ /I ₁₁₀₆ | I ₁₁₇₄ /I ₇₈₀ | I ₁₁₇₄ /I ₁₁₀₆ | I ₁₁₇₄ /I ₄₃₆ |
|--------------------------------------|------------|------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|--------------------------------------|-------------------------------------|
| -105 | 5.947 | _ | 7.247 | 1.635 | 3.268 | 0.737 | _ |
| -110 | 6.129 | 4.943 | 7.374 | 1.721 | 3.348 | 0.781 | 6.220 |
| -115 | 6.323 | 5.002 | _ | 1.722 | 3.426 | 0.800 | 6.778 |
| -120 | 6.530 | - | 7.499 | 1.736 | 3.495 | 0.809 | 6.954 |
| -125 | 6.750 | 5.924 | _ | 1.766 | 3.559 | 0.848 | - |
| -130 | 6.986 | 6.224 | 7.545 | 1.797 | 3.713 | 0.885 | 7.532 |
| -135 | 7.239 | - | 7.833 | 1.852 | 3.856 | 0.912 | 7.664 |
| -140 | 7.510 | 6.651 | _ | _ | 4.069 | 0.983 | 7.825 |
| -145 | 7.803 | 7.028 | 8.355 | 1.952 | 4.402 | 1.028 | 8.259 |
| -150 | 8.120 | 7.257 | 9.021 | 2.100 | 4.723 | 1.099 | _ |
| $\Delta H^{\rm b} \ ({\rm cm}^{-1})$ | | 139 ± 14 | 63 ± 10 | 69 ± 6 | 115 ± 7 | 122 ± 4 | 105 ± 11 |

^a The first frequency is from the Me-trans conformer.

^b Average value of ΔH is 102 ± 6 cm⁻¹ (1.21 ± 0.07 kJ mol⁻¹) for Me-*trans*/F-*trans* conformers with the Me-*trans* more stable.

| 83 | 7 |
|----|---|
| | |

| Table 7 | | | | | | | | | | | | | | | |
|-------------|-----|-----------|--------|------|-----|----------------|-------|-------|-----------|-------|---------|------------|------------|-----------------------|--|
| Temperature | and | intensity | ratios | from | the | conformational | study | of th | e Me-tran | s and | H-trans | conformers | in krypton | solution ^a | |

| <i>T</i> (°C) | 1000/T (K) | I ₄₅₇ /I ₅₈₈ | I ₁₃₀₃ /I ₅₈₈ | I_{1174}/I_{588} | <i>I</i> ₁₁₇₄ / <i>I</i> ₇₉₄ | I_{1174}/I_{418} | I ₄₅₇ /I ₄₁₈ |
|------------------------------------|------------|------------------------------------|-------------------------------------|--------------------|----------------------------------------------------|--------------------|------------------------------------|
| -105 | 5.947 | 15.677 | 4.339 | 7.069 | 7.061 | 1.144 | 2.536 |
| -110 | 6.129 | 18.879 | _ | 8.571 | 7.306 | 1.212 | 2.669 |
| -115 | 6.323 | _ | 5.151 | _ | 7.956 | 1.282 | 2.757 |
| -120 | 6.530 | 20.248 | 5.302 | 9.438 | 8.061 | 1.431 | 3.069 |
| -125 | 6.750 | _ | - | 9.674 | 7.956 | 1.576 | 3.283 |
| -130 | 6.986 | 22.321 | 5.800 | 10.986 | 8.037 | 1.639 | 3.330 |
| -135 | 7.239 | 23.662 | 5.951 | 11.649 | 9.216 | 1.782 | 3.619 |
| -140 | 7.510 | _ | 7.648 | _ | 10.124 | 1.971 | _ |
| -145 | 7.803 | 29.894 | - | 15.750 | 12.039 | 2.130 | 4.043 |
| -150 | 8.120 | 34.336 | 8.086 | _ | 13.015 | 2.232 | 4.262 |
| $\Delta H^{\rm b}~({\rm cm}^{-1})$ | | 224 ± 18 | 207 ± 2 | 269 ± 23 | 190 ± 20 | 223 ± 9 | 169 ± 9 |

^a The first frequency is from the Me-trans conformer.

^b Average value of ΔH is $208 \pm 8 \text{ cm}^{-1}$ ($2.49 \pm 0.10 \text{ kJ mol}^{-1}$) for Me-*trans*/H-*trans* conformers with the Me-*trans* more stable.

calculations. Several bands in the region between 380 and 430 cm^{-1} in the infrared spectrum of the gas also disappeared in the solid with two of them arise from the fundamentals of the H-*trans* conformer and one from the F-*trans* conformer. Therefore, it is clear that only the Me-*trans* form exists in the polycrystalline solid. Thus, all bands in the spectrum of the solid are assigned to the Me-*trans* conformer. Since the Me-*trans* form is predicted as the most stable conformer by all MP2 calculations in this study, most of bands observed in the fluid states are assigned to this conformer which is consistent with the previous investigations [5].

The assignment of carbon-hydrogen stretching modes is straightforward on the basis of the scaled ab initio predicted frequencies and well known "group frequencies". Eight *Q*-branches in the spectrum of the gas and seven bands in the spectrum of solid are assigned to $v_1 - v_9$ fundamentals for the Me-trans conformer. However, the Q-branch at 2952 cm^{-1} has to be assigned to the CH₂ antisymmetric stretching fundamental for the F-*trans* form (v'_5 where the single and double primes indicate the F-trans and H-trans conformers, respectively), since it disappeared in the spectrum of the annealed solid. The fundamentals v_{10} , v_{11} , and v_{12} , which were not assigned previously, are assigned to doublets at 1479 (1473), 1467 (1465), and 1462 (1458) cm^{-1} in the spectrum of the solid, where the numbers in the parentheses are due to factor group splitting in the solid. The CH₂ twisting fundamentals with the predicted frequencies of 1275, 1272, and 1263 cm^{-1} are assigned to the infrared bands at 1278, 1271, and 1264 cm^{-1} for the H-*trans*, Me-trans, and F-trans conformers, respectively, with the first and the third band vanishing in the spectrum of the solid. The CH₃ rocking fundamental for the H-*trans* form, v_{22}'' , is assigned to a strong Q-branch (C-type band) at 1112 cm^{-1} in the infrared spectrum of the gas and a band at $1103 \,\mathrm{cm}^{-1}$ in the Raman spectrum of liquid which is in agreement with the previous reported assignment [5]. The C-F stretches were predicted at 909, 905, and 900 cm⁻¹ with strong infrared intensities and they are assigned to strong bands at 905, 899,

and 894 cm⁻¹ for the F-trans, Me-trans, and H-trans conformers, respectively. However, only one Raman band at $898 \,\mathrm{cm}^{-1}$ was observed in the spectrum of liquid and it is assigned to this mode for all three conformers. The $C_1C_2C_3$ bending fundamental of the H-trans conformer with the infrared intensity of $2.0 \,\mathrm{km \, mol^{-1}}$ is assigned to a weak but well defined band at 588 cm^{-1} in the spectrum of the krypton solution. The corresponding fundamentals for the Me-trans and F-*trans* conformers are observed at 493 and $436 \,\mathrm{cm}^{-1}$. respectively, in the same spectrum. The CCF out-of-plane and in-plane bends are assigned to bands at 457, $369 \,\mathrm{cm}^{-1}$ and 488, 398 cm⁻¹ for the Me-trans and F-trans conformers, respectively. However, only the in-plane mode ν_{32}'' was observed at 420 cm^{-1} for the highest energy H-*trans* form. Two bands with C- and A-type band contours are observed at 255 and 243 cm⁻¹, which are assigned to the v_{34} and v_{35} fundamentals for the Me-trans conformer. Additionally, the asymmetric torsional mode is assigned to a broad band centered at $108 \,\mathrm{cm}^{-1}$ in the far infrared spectrum of the gas (Fig. 2). The assignments for the observed fundamentals of 2-fluorobutane are listed in Tables 1-3 for the Me-trans, F-trans, and H-trans conformers, respectively.

5. Conformational stability

There are three stable conformers in the fluid states and many fundamentals have nearly the same frequencies, but bands due to each single conformer can still be identified. As mentioned earlier, a series of bands disappeared in the spectrum of the polycrystalline solid which must arise from either the F-*trans* or H-*trans* conformer. Aided by the normal coordinate analysis, many of those bands can be confidently assigned. For example, the predicted frequencies of v_{28}'' (H-*trans*) and v_{29}' (F-*trans*) fundamentals are 790 and 771 cm⁻¹ with the infrared intensities of 3.1 and 3.5 km mol⁻¹, respectively, are assigned to two weak bands at 794 and 780 cm⁻¹ in the spectra of the krypton solution. Therefore, there were several bands for each conformer



Fig. 6. Mid-infrared spectra of 2-fluorobutane dissolved in liquid krypton at -125 °C. (MeT, FT, and HT indicate the Me-*trans*, F-*trans*, and H-*trans* conformer, respectively.)

which could be used for the enthalpy difference determinations (Fig. 6).

Six Me-*trans*/F-*trans* and six Me-*trans*/H-*trans* conformer pairs were utilized in this study to determine the enthalpy differences. The spectra were recorded at temperatures from -105 to -150 °C with the sample dissolved in the liquefied krypton. The partial spectra of the krypton solution at different temperatures (Fig. 7), with the bands at 493 and 457 cm⁻¹ due to the Me-*trans* form and the bands at 588 and 418 cm⁻¹ for the H-*trans* conformer and bands at 490 and 436 due to the F-*trans* form, show increased



Fig. 7. Temperature dependent infrared spectrum of 2-fluorobutane in liquid krypton (400–530 cm⁻¹) in the temperature from -105 to -145 °C.

intensity for the Me-trans conformer as the temperature decreases, which is consistent with the ab initio energy predictions. The natural logarithm of the ratio of the intensities of each conformer pair were plotted against the reciprocal of absolute temperature and these data points were fitted to the equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$. The ΔH values were determined from van't Hoff plot of $-\ln K$ versus 1/Twhere $\Delta H/R$ is the slope of the fitted line and intensity ratios of conformer bands were substituted for K. It is assumed that ΔH is not a function of temperature over the relatively small temperature range. The determined ΔH values ranged from a high of 139 ± 14 cm⁻¹ to a low of 63 ± 10 cm⁻¹ with an average of $102 \pm 6 \text{ cm}^{-1}$ $(1.21 \pm 0.07 \text{ kJ mol}^{-1})$ with the Me-trans conformer more stable than the F-trans form. Similarly, the average enthalpy difference between the Me-trans and H-trans forms was determined to be $208 \pm 8 \text{ cm}^{-1}$ (2.49 ± 0.10 kJ mol⁻¹) with the Me-*trans* form being more stable. These enthalpy differences should be close to the value in vapor state [18-22], since the three conformers have similar molar volumes and their dipole moments differ by less than 10%. The uncertainties in these values are the statistical uncertainties which do not take into account factors such as the presence of overtone or combination bands in near coincidence with the measured fundamentals. Therefore, a more realistic value for the uncertainty should be at least 10% which results in values of $102 \pm 10 \text{ cm}^{-1}$ (1.21 ±0.1.12 kJ mol⁻¹) and $208 \pm 21 \text{ cm}^{-1}$ $(2.49 \pm 0.25 \text{ kJ mol}^{-1})$ for the enthalpy differences for the Me-trans/F-trans and Me-trans/H-trans pairs. By utilizing the experimentally determined enthalpy differences in the present study, the estimated abundances for the Me-trans, F-trans, and H-trans conformers at ambient temperature are 50 ± 2 , 31 ± 1 , and $19 \pm 1\%$, respectively.

6. Disscusion

The average values of ΔH of $102 \pm 10 \,\mathrm{cm}^{-1}$ between the Me-trans and F-trans forms and $208 \pm 21 \,\mathrm{cm}^{-1}$ between the Me-trans and H-trans forms with the Me-trans form the most stable conformer shows that the ab initio MP2/6-311+G(2d, 2p) calculations with the predicted energy differences of 156 and 214 cm⁻¹ for Me-trans/F-trans and Me-trans/H-trans pairs are reasonably good predictions. However, the MP2/6-31G(d) calculations gave incorrect predictions on the relative stabilities of the second and third stable conformers, i.e. F-trans and H-trans forms, with the H-*trans* conformer more stable by 31 cm^{-1} which is contrary to the experimental results. Ab initio calculations may give the incorrect results when smaller basis sets are employed and the credibility of the conformational stability predictions decreases if the energy difference between the conformers is less than $100 \,\mathrm{cm}^{-1}$. For example, the ab initio calculations for both 1-chloropropane and 1-bromopropane resulted in the wrong predictions when the smaller basis sets were utilized [2]. The RHF/6-31G(d) and B3LYP/6-31G(d) calculations gave the correct predictions on the conformational stabilities, but the value of the energy differences are too high (Table 4, B3LYP results not listed). Therefore, the second order perturbation level calculations with larger basis sets are preferred for obtaining reliable predictions on the conformational behavior of the alkyl halides such as 2-fluorobutane. Nevertheless, experimental enthalpy determinations are frequently necessary to verify the theoretical predictions.

In the previous vibrational study of this molecule [5], only a few bands were assigned to the high energy F-trans and H-trans forms. Many of the fundamentals in the "fingerprint" region have been assigned for the F-trans conformer and several bands are also identified for the H-trans conformer in the present study. For example, the C_2C_3 stretch and the CH₂ twisting fundamentals $(v_{28}'' \text{ and } v_{29}')$ for the H-*trans* and F-trans conformers, respectively, were not reported previously in the Raman spectrum of liquid. These two fundamentals, with predicted values of 790 and 771 cm^{-1} , are assigned to the Raman lines at 795 and 782 cm⁻¹, respectively. The v_{30}'' and v_{30}' fundamentals for the H-*trans* and F-trans conformers are assigned to the two weak bands at 588 and $433 \,\mathrm{cm}^{-1}$, respectively, in the infrared spectrum of the krypton solution. These assignments facilitated the enthalpy determinations, since values derived from multiple pairs produce more reliable results.

The infrared bands at 494 and 461 cm^{-1} in the spectrum of the solid were assigned to the Me-trans and F-trans conformers, respectively, in the previous study [5]. This assignment led to the conclusion that the Me-trans and F-trans conformers coexist in the polycrystalline solid. However, the assignment presented herein shows that the second band is the v_{31} fundamental for the Me-trans conformer with the predicted value of 459 cm⁻¹. The calculated values for bands in this region for the F-trans conformer are 482 cm^{-1} for v'_{31} which is too high and 432 cm^{-1} for v'_{30} which is too low. Eight fundamentals from the F-*trans* conformer $(\nu'_{20}, \nu'_{22},$ $v'_{27} - v'_{32}$) and six fundamentals from the H-*trans* conformer $(v_{20}'', v_{26}'' - v_{28}'', v_{30}'', \text{ and } v_{32}'')$ disappeared from the spectrum of the solid with annealing. Therefore, it is very clear that the Me-trans form is the only conformer remaining in the crystalline solid. Many bands in the spectrum of the crystalline solid show factor group splitting such as the $v_{10} - v_{14}$, $v_{24} - v_{27}$, v_{29} , v_{30} , and v_{32} fundamentals which are observed as doublets. Therefore, at least two molecules must exist per unit cell in the crystal.

Most structural parameters obtained from the MP2/6-311 +G(d, p) calculations are similar among the three conformers. However, some significant differences arise from the backbone structure. The C₁C₂ bond distances between the F-*trans* and H-*trans* forms differ by 0.004 Å with the H-*trans* form having the larger value and its C₂C₃ bond distance is also larger than the corresponding bond distances for the Me-*trans* and F-*trans* forms by 0.004 and 0.002 Å, respectively. The C₃C₄ and CF bond distances and all carbon hydrogen bond distances are nearly the same among the three

conformers. The largest difference among the angles is for $\angle C_1 C_2 C_3$ with the value for H-*trans* conformer 1.3° larger than those for the other two conformers. The $\angle C_2 C_3 C_4$ for the H-trans form is larger by 1.2° and 0.5° than the corresponding angles for the Me-trans and F-trans forms, respectively. Additionally, the $\angle C_2C_3F$ of the F-trans form is less than the other two conformers by 0.5°. Compared with the fluorine and hydrogen atoms, the methyl group is much larger, and therefore, the values of the $\angle C_2C_3C_4$ for the H-trans and F-trans forms are slightly larger than the corresponding angle of the Me-trans conformer where the two methyl groups are in the gauche position. For the H-trans conformer, both the fluorine and methyl group are in the gauche positions to the first methyl group which generates maximum steric hindrance and consequently, the value of $\angle C_2 C_3 C_4$ is the largest among the three forms. This steric factor has practically no effect on the hydrogen atom and the values of $\angle C_2C_3H_9$ which are essentially the same among the three conformers.

All three conformers of 2-fluorobutane have only trivial C₁ symmetry. Therefore, the PEDs involve extensive mixing of the symmetry coordinates. For example, the *CH₃ rocking fundamental (asterisk indicates carbon-1) for the Me-trans conformer (ν_{26}) only has 11% contribution from the described atomic motion. The CH₃ rocking fundamental (ν_{21}) is extensively mixed and no contribution has a value greater than 20% (Table 1). However, fundamentals for the carbon hydrogen stretches and torsional modes are much purer with the major contributions more than 60%. The situations for the F-trans and H-trans conformers are almost the same and one-half of the 36 fundamentals have major contributions less than 50%. Therefore, the descriptions given to the normal modes are more for book-keeping than to give the atom motions for the fundamentals, especially in the fingerprint region.

The predicted potential function (Fig. 8) has been plotted from the data obtained from the MP2/6-311+G(d, p) calculations with full geometry optimization at the three transition states as well as the three stable potential minima and a subsequent fit of the energies to an asymmetric potential of the type:

$$V(\phi) = \sum_{i=1}^{3} \left(\frac{V_i}{2}\right) (1 - \cos i\phi) + \sum_{i=1}^{3} \left(\frac{V'_i}{2}\right) \sin i\phi.$$

where ϕ and *i* are the torsional angle and foldness of the barrier, respectively. The potential coefficients, V_1 , V_2 , V_3 and V'_1 , V'_2 , and V'_3 along with torsional transitional barriers are listed in Table 8. On the basis of our experience with other molecules, [1,2,9], it is expected that the barriers between the F-*trans* and H-*trans* forms are slightly larger than the experimental values.

In the previous vibrational study of *n*-butane, the *trans* conformer is more stable with an enthalpy difference of 245 cm^{-1} [3]. For the 1-halo substituted propanes, the *gauche* form is the more stable conformer with enthalpy

| Parameter | Potential coefficient | Torsional transition | Potential barrier | |
|----------------------------------------------------------|-----------------------|-----------------------------------|-------------------|--|
| V1 | 394 | Me-trans \rightarrow F-trans | 1249 | |
| V_2 | -138 | Me-trans \rightarrow H-trans | 1719 | |
| V_3 | 1518 | F -trans \rightarrow H-trans | 1847 | |
| V_1' | -303 | F -trans \rightarrow Me-trans | 1103 | |
| V_2' | -224 | H -trans \rightarrow Me-trans | 1511 | |
| $V_3^{\tilde{\prime}}$ | 196 | H-trans \rightarrow F-trans | 1785 | |
| ΔE (Me-trans \rightarrow H-trans) | 208 | | | |
| $\Delta E \text{ (Me-trans} \rightarrow \text{F-trans)}$ | 146 | | | |

Table 8 Potential barriers and coefficients (cm⁻¹) of 2-fluorobutane^a

^a From MP2/6-311+G(d, p) ab initio calculations.

differences of 100, 52, and 72 cm^{-1} for the fluoride [1], chloride, and bromide [2], respectively. Based on these experimental results, the Me-trans form is expected to be more stable if both the methyl group and halogen atom are on the same atom. For 2-chlorobutane and 2-bromobutane, the electron diffraction studies [4] indicated that the Me-trans form is the lowest energy conformer whereas the H-trans and Br-trans forms are the highest energy forms for the chloride and bromide, respectively. However, studies from temperature dependent infrared spectra in krypton solution utilizing seven conformer pairs for both the chloride and bromide showed the H-trans conformer as the highest energy form for both molecules with the enthalpy differences of 223 and 226 cm⁻¹, respectively, between the Me-trans and halo-trans forms [23,24]. Similar results were obtained for butyronitrile [6] and 2-methylbutyronitrile [8] where the gauche and Me-trans forms are the lowest energy forms, respectively. For 3-methyl-1-pentyne, the Me-trans form was predicted as the more stable from the MM2 calculations but the trans conformer for 1-pentyne [7] is experimentally determined to be more stable by $113 \,\mathrm{cm}^{-1}$ from the krypton solution. Most of the substituents, including halogen



Fig. 8. Potential function governing the internal rotation of 2-fluorobutane as determined by ab initio calculations (MP2/6-311+G(d, p)).

atoms, have lone pair electrons and the hyperconjugation between the methyl group and the substituents is believed to be the major factor which causes the *halo-trans* form to be less stable where the distance between the methyl group and substitute is large. The CN and C=C groups are also electron-rich moieties and we expect the same hyperconjugation effects exist and consequently, the Me-*trans* form with the substitutents *gauche* to the methyl group is the most stable form. Compared with the electronic effects, the steric factor is probably less important for these kinds of molecules. For instance, the Me-*trans* form for 2-bromobutane is more stable even though the Br atom has a much larger size than the methyl group.

Acknowledgements

JRD acknowledges the University of Missouri-Kansas City for a Faculty Research grant for partial financial support of this research. The authors thank Sergio Moore for carrying out most of the initial ab initio calculations.

References

- [1] G.A. Guirgis, X. Zhu, J.R. Durig, Struct. Chem. 10 (1999) 445.
- [2] J.R. Durig, X. Zhu, S. Shen, J. Mol. Struct. 570 (2001) 1.
- [3] H.D. Stidham, J.R. Durig, Spectrochim. Acta A 42 (1985) 105.
- [4] K. Aarset, K. Hagen, R. Stolevik, J. Mol. Struct. 567 (2001) 157.
- [5] G.A. Crowder, T. Koger, J. Mol. Struct. 29 (1975) 233.
- [6] G.A. Crowder, G.O. Carlisle, J. Comp. Chem. 12 (1991) 880.
- [7] S. Bell, G.A. Guirgis, Y. Lin, J.R. Durig, J. Phys. Chem. A 101 (1997) 5987.
- [8] J.R. Durig, B.R. Drew, A. Koomer, S. Bell, Phys. Chem. Chem. Phys. 3 (2001) 766.
- [9] J.R. Durig, X. Zhu, G.A. Guirgis, S. Bell, J. Mol. Struct., submitted for publication.
- [10] W.F. Edgell, L. Parts, J. Am. Chem. Soc. 77 (1955) 4899.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V.

Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A.7), Gaussian Inc., Pittsburgh, PA, 1998.

- [12] P. Pulay, Mol. Phys. 17 (1969) 197.
- [13] G.A. Guirgis, X. Zhu, Z. Yu, J.R. Durig, J. Phys. Chem. A 104 (2000) 4383.
- [14] M.J. Frisch, Y. Yamaguchi, J.F. Gaw, H.F. Schaefer III, J.S. Binkley, J. Chem. Phys. 84 (1986) 531.
- [15] R.D. Amos, Chem. Phys. Lett. 124 (1986) 376.
- [16] P.L. Polavarapu, J. Phys. Chem. 94 (1990) 8106.

- [17] G.W. Chantry, in: A. Anderson (Ed.), The Raman Effect, vol. 1, Marcel Dekker, New York, 1971 (Chapter 2).
- [18] W.A. Herrebout, B.J. van der Veken, J. Phys. Chem. 100 (1996) 9671.
- [19] M.O. Bulanin, Mol. Struct. 19 (1973) 59.
- [20] B.J. van der Veken, E.R. DeMunck, J. Chem. Phys. 97 (1992) 3060.
- [21] W.A. Herrebout, B.J. van der Veken, A. Wang, J.R. Durig, J. Phys. Chem. 99 (1995) 578.
- [22] M.O. Bulanin, J. Mol. Struct. 347 (1995) 73.
- [23] X. Zhu, S. Shen, W.A. Herrebout, B.J. van der Veken, J.R. Durig, J. Mol. Struct., submitted for publication.
- [24] J.R. Durig, S. Shen, W.A. Herrebout, B.J. van der Veken, J. Phys. Chem. A, submitted for publication.