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# Raman and Infrared Spectra, Conformational Stability, Barriers To Internal Rotation, Normal Coordinate Analysis, Vibrational Assignment, and ab Initio Calculations of 3,3-Difluoropropene

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The Raman spectra (3500 to 40 $\text{cm}^{-1}$) of gaseous, liquid, and solid 3,3-difluoropropene, $CH_2CHCF_2H$, and the infrared spectra (3500 to 60 $\text{cm}^{-1}$) of the gas and solid have been recorded. The spectra of the fluid phases are consistent with two stable conformers in equilibrium at ambient temperature. The mid-infrared spectra of the sample dissolved in liquid xenon as a function of temperature (−55 to −100 °C) have been recorded. Utilizing two conformer pairs, the enthalpy difference has been determined to be 82 ± 10 $\text{cm}^{-1}$ (0.98 ± 0.12 kJ/mol) with the cis conformer (H atom of the difluoromethyl group is cis to the double bond) the more stable form. The cis conformer is also the more stable form in the liquid, and it is the only rotamer present in the solid. The first overtone of the asymmetric torsion for the cis conformer was observed at 179.6 $\text{cm}^{-1}$ with four successive excited-state overtones observed falling to lower frequency. The corresponding fundamental for the gauche conformer was observed at 97.65 $\text{cm}^{-1}$ with three excited states falling to lower frequency. Utilizing these torsional data along with the experimental enthalpy and gauche dihedral angle, the potential function governing the conformational interchange has been determined and the potential coefficients are $V_1 = 215 \pm 16$, $V_2 = -111 \pm 17$, $V_3 = 633 \pm 6$, $V_4 = 54 \pm 8$, $V_5 = -25 \pm 4$, and $V_6 = -12 \pm 2$ $\text{cm}^{-1}$. The gauche to cis barrier is 560 $\text{cm}^{-1}$ (6.70 kJ/mol) and the gauche to gauche barrier is 744 $\text{cm}^{-1}$ (8.90 kJ/mol). The vibrational assignment for the 21 normal modes for the cis conformer is proposed and several of the fundamentals for the gauche conformer have been identified. The structural parameters, dipole moments, conformational stability, vibrational frequencies, infrared intensities, and Raman activities have been obtained from ab initio calculations, and the predicted conformational stability is consistent with the experimental results. These experimental and theoretical results are compared to the corresponding quantities of some similar molecules.

## Introduction

We have carried out extensive studies on the conformational stability of the allyl halides (3-halopropenes) over the years, and it has been found that only the allyl fluoride molecule has the cis conformer as the more stable rotamer.[1−8] Similar studies have been carried out for the halomethylcyclopropane molecules,[9−15] which are frequently used for comparison since the three-membered ring has some bonding properties similar to those in the ethylene group. Unfortunately, the conformational stability of the fluoromethylcyclopropane molecule has not been determined.[16,17] As a continuation of our studies on these types of molecules, we recently determined the conformational stability of difluoromethylcyclopropane,[18] which is the first dihalomethylcyclopropane molecule studied for the purpose of determining the conformational stability. From the infrared and Raman spectral investigation of this molecule it was determined that the cis (H atom of the difluoromethyl group is cis to the three-membered ring) is more stable than the gauche form in both the gaseous and liquid phases and it is the only rotamer present in the solid. The enthalpy difference was determined to be 102 ± 8 $\text{cm}^{-1}$ (1.22 ± 0.10 kJ/mol) from the mid-infrared spectra of the sample dissolved in liquid xenon as a function of temperature. As a continuation of these studies, we have investigated the infrared and Raman spectra of 3,3-difluoropropene, $CH_2CHCF_2H$, for the purpose of determining its conformational stability for comparison with the corresponding substituted three-membered ring.

There have been no previous vibrational spectroscopic studies of 3,3-dihalopropene, so we have recorded the Raman spectra of the gas, liquid, and solid and the infrared spectra of the gas, xenon solutions at variable temperature, and solid. We have also carried out ab initio calculations employing the 6-31G(d) basis set at a level of restricted Hartree−Fock (RHF) and Moller−Plesset to second order (MP2) to obtain equilibrium geometries, force constants, vibrational frequencies, infrared intensities, Raman activities, and conformational stabilities. Structural parameters and conformational stabilities have also been obtained from larger basis sets, i.e., MP2/6-311+G(d,p) and MP2/6-311+G(2d,2p). The results of this vibrational spectroscopic and theoretical study are reported herein.

## Experimental Section

The 3,3-difluoropropene sample was provided by Bayer Corp., Charleston, SC. The sample was purified by using a low-temperature, low-pressure fractionation column and the sample was stored at low temperature under vacuum until used. The

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**TABLE 1: Structural Parameters, Rotational Constants, Dipole Moments, and Total Energies for 3,3-Difluoropropene**[a]

| | internal | RHF/6-31G(d) | | MP2/6-31G(d) | | MP2/6-311+G(d,p) | | adjusted $r_o$ | | MP2/6-311+G(2d,2p) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| parameter[b] | coordinates | cis | gauche | cis | gauche | cis | gauche | cis | gauche | cis | gauche |
| $r(C_2-H_1)$ | $r_1$ | 1.074 | 1.074 | 1.084 | 1.084 | 1.084 | 1.084 | 1.084 | 1.084 | 1.077 | 1.077 |
| $r(C=C)$ | $S$ | 1.316 | 1.316 | 1.335 | 1.334 | 1.338 | 1.337 | 1.335 | 1.337 | 1.331 | 1.331 |
| $r(C_3-H_4)$ | $r_3$ | 1.076 | 1.076 | 1.086 | 1.086 | 1.087 | 1.087 | 1.086 | 1.086 | 1.080 | 1.080 |
| $r(C_2-H_5)$ | $r_2$ | 1.077 | 1.074 | 1.086 | 1.083 | 1.086 | 1.084 | 1.085 | 1.084 | 1.079 | 1.077 |
| $r(C-C)$ | $T$ | 1.491 | 1.495 | 1.484 | 1.491 | 1.486 | 1.493 | 1.482 | 1.492 | 1.482 | 1.488 |
| $r(C_6-H_7)$ | $r_4$ | 1.078 | 1.080 | 1.094 | 1.094 | 1.092 | 1.093 | 1.091 | 1.093 | 1.085 | 1.086 |
| $r(C_6-F_8)$ | $P$ | 1.346 | 1.347 | 1.374 | 1.376 | 1.370 | 1.372 | 1.368 | 1.372 | 1.370 | 1.373 |
| $r(C_6-F_9)$ | $Q$ | 1.346 | 1.342 | 1.374 | 1.370 | 1.370 | 1.363 | 1.368 | 1.362 | 1.370 | 1.364 |
| $\angle(H_1C_2C_3)$ | $\pi_1$ | 121.7 | 121.1 | 121.8 | 121.1 | 121.5 | 120.7 | 121.6 | 120.7 | 121.4 | 120.7 |
| $\angle(H_4C_3C_2)$ | $\epsilon_1$ | 121.9 | 121.5 | 122.2 | 121.8 | 122.3 | 121.6 | 122.4 | 121.6 | 122.2 | 121.5 |
| $\angle(H_5C_2H_1)$ | $\delta$ | 116.4 | 117.0 | 116.6 | 117.5 | 117.0 | 117.8 | 117.0 | 117.8 | 117.6 | 118.3 |
| $\angle(C_6C_3C_2)$ | $\epsilon_2$ | 122.8 | 124.0 | 122.0 | 123.0 | 121.7 | 123.5 | 122.4 | 123.3 | 121.7 | 123.4 |
| $\angle(H_7C_6C_3)$ | $\phi$ | 113.3 | 112.8 | 113.6 | 113.8 | 114.0 | 113.8 | 113.9 | 113.8 | 113.6 | 113.8 |
| $\angle(F_8C_6F_9)$ | $\eta$ | 106.5 | 107.6 | 106.8 | 107.7 | 106.5 | 107.3 | 106.3 | 107.0 | 106.4 | 107.4 |
| $\tau(H_7C_6C_3C_2)$ | $\tau$ | 0.0 | 112.4 | 0.0 | 113.0 | 0.0 | 113.0 | 0.0 | 113.1 | 0.0 | 114.1 |
| $A$ | | 9378 | 9144 | 8995 | 8811 | 9060 | 8872 | 9124 | 8902 | 9081 | 8867 |
| $B$ | | 3759 | 4235 | 3727 | 4215 | 3717 | 4185 | 3721 | 4193 | 3739 | 4220 |
| $C$ | | 2992 | 3143 | 2941 | 3107 | 2942 | 3096 | 2948 | 3107 | 2955 | 3121 |
| $\lvert\mu_a\rvert$ | | 2.346 | 1.638 | 2.533 | 1.735 | 2.823 | 2.031 | 2.369(15) | 1.535(15) | 2.705 | 1.910 |
| $\lvert\mu_b\rvert$ | | 0.000 | 0.730 | 0.000 | 0.793 | 0.000 | 0.771 | 0.0 | 0.53(4) | 0.000 | 0.752 |
| $\lvert\mu_c\rvert$ | | 0.740 | 1.356 | 0.773 | 1.449 | 0.885 | 1.512 | 0.70(3) | 1.36(3) | 0.835 | 1.460 |
| $\lvert\mu_t\rvert$ | | 2.460 | 2.248 | 2.648 | 2.395 | 2.958 | 2.647 | 2.47(3) | 2.12(5) | 2.834 | 2.519 |
| $-(E+314)$ | | 0.782282 | 0.781986 | 1.518040 | 1.518031 | 1.774363 | 1.773149 | | | 1.888941 | 1.887834 |
| $\Delta E/cm^{-1}$ | | | 65 | | 2 | | 266 | | 260 ± 80 | | 243 |

[a] Bond lengths in angstroms, bond angles in degrees, rotational constants in megahertz, dipole moments in debyes, and energies in hartrees. [b] $H_1$ is cis to $C_6$ atom.

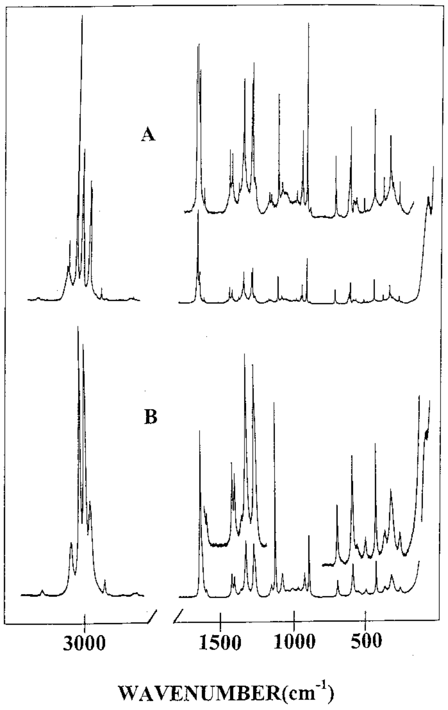

**Figure 1.** Raman spectra of 3,3-difluoropropene: (A) gas; (B) liquid.

purity of the sample was checked by comparing the mid-infrared spectrum with that predicted by ab initio calculations and the NMR and mass spectral data. All sample transfers were carried out under vacuum to avoid contamination.

The Raman spectra of 3,3-difluoropropene from 3500 to 40 cm$^{-1}$ were recorded on a Cary model 82 spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The spectrum of the gas was recorded using a standard Cary multipass accessory. The spectrum of the liquid was recorded from the sample contained in a Pyrex capillary with a bulb on the end,[19] and representative Raman spectra of the gas and the liquid are shown in Figure 1.

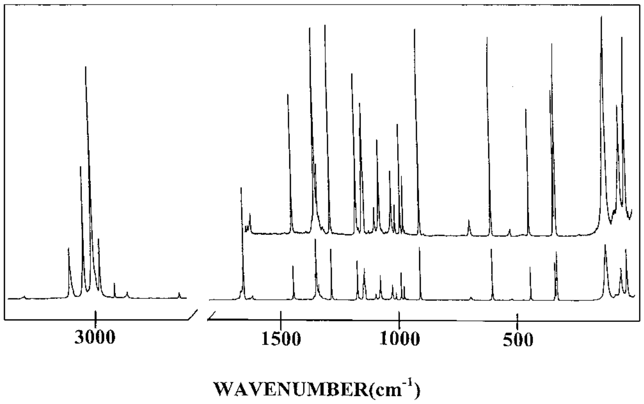

**Figure 2.** Raman spectra of 3,3-difluoropropene in annealed solid.

The spectrum of the annealed solid (Figure 2) was obtained by depositing the sample on a blackened brass block which was maintained in a cell fitted with quartz windows and cooled with boiling liquid nitrogen. The frequencies for all the observed lines are listed in Table 1S.

The mid-infrared spectra (Figure 3) of the gas and the annealed solid from 3500 to 400 cm$^{-1}$ were recorded with a Digilab model FTS-14C Fourier transform spectrometer equipped with a Globar source, a Ge/KBr beam splitter, and a triglycine sulfate (TGS) detector. The spectrum of the gas was obtained with the sample contained in a 10 cm cell equipped with CsI windows. Atmospheric water vapor was removed from the spectrometer by purging with dry nitrogen. For the solid, the spectrum was recorded by depositing a sample film onto a CsI substrate cooled by boiling liquid nitrogen and housed in a vacuum cell fitted with CsI windows. The sample was annealed until no further changes were observed in the spectrum.

The far-infrared spectrum (500 to 30 cm$^{-1}$) of the solid (Figure 4) was obtained by using a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a far-infrared grid beam splitter and a DTGS detector. The spectrum was obtained by condensing the sample on to a silicon plate held in a cell

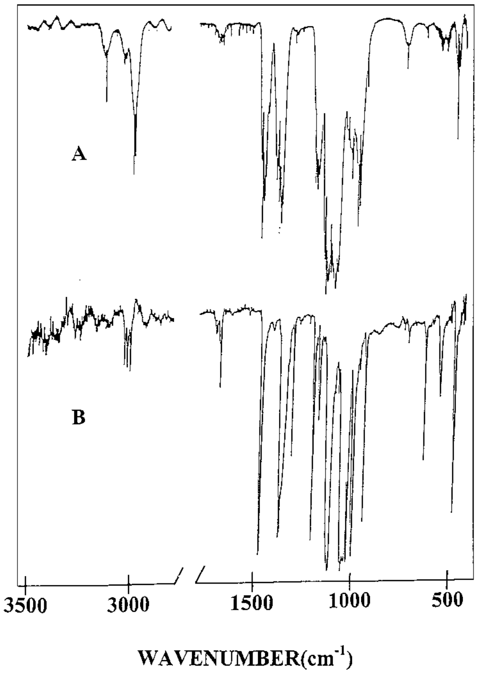

**Figure 3.** Mid-infrared spectra of 3,3-difluoropropene: (A) gas; (B) annealed solid.

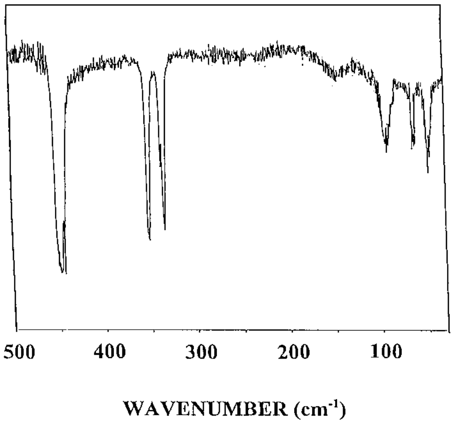

**Figure 4.** Far infrared spectrum of 3,3-difluoropropene in the region of 500 to 30 cm$^{-1}$ in annealed solid.

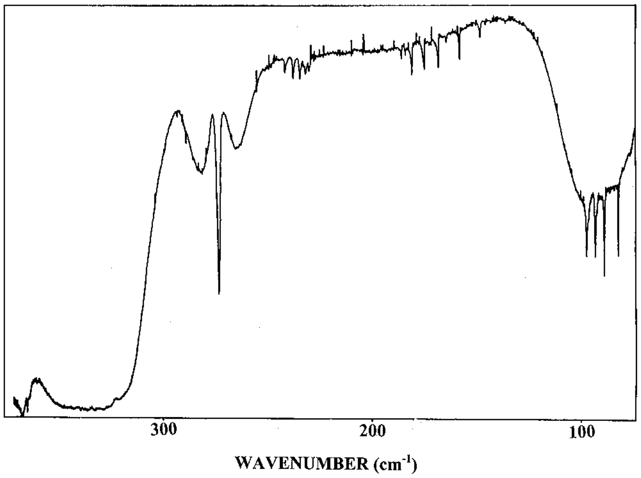

**Figure 5.** Far infrared spectrum of 3,3-difluoropropene in the region of 380 to 50 cm$^{-1}$ in gas.

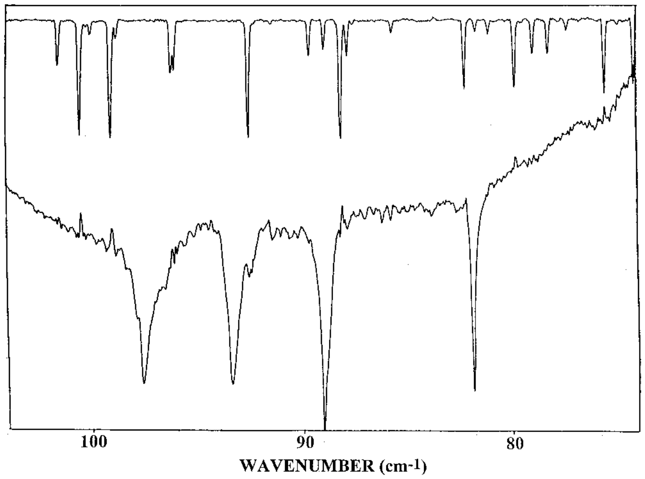

**Figure 6.** Far infrared spectrum of 3,3-difluoropropene in the region of 104 to 74 cm$^{-1}$ in gas.

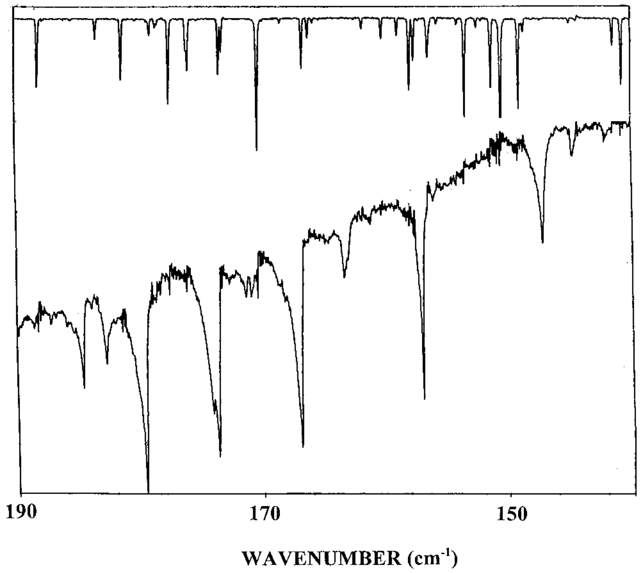

**Figure 7.** Far infrared spectrum of 3,3-difluoropropene in the region of 190 to 140 cm$^{-1}$ in gas.

equipped with polyethylene windows and cooled with boiling liquid nitrogen. The sample was annealed until no further changes were observed in the spectrum.

The far infrared spectrum (Figures 5−7) of the gas from 380 to 50 cm$^{-1}$, from which the torsional transitions were measured (Figure 6), was recorded on a Nicolet model 200 SXV Fourier transform interferometer equipped with a vacuum bench, Globar source, liquid helium cooled Ge bolometer with a wedged sapphire filter and polyethylene windows. Traces of water in the sample were removed by passing the gas through activated 3 Å molecular sieves, using standard vacuum techniques. The gas was contained in a 1 m folded path cell with polyethylene windows. A 6.25 $\mu$m Mylar beam splitter was used to record the spectra at a resolution of 0.08 cm$^{-1}$. Typically, 256 scans were used for both the sample and reference data, averaged, and transformed with a boxcar truncation function to give a satisfactory signal-to-noise ratio.

The mid-infrared spectra of the sample dissolved in liquified xenon (Figure 8A) were recorded on a Bruker model IFS-66 Fourier interferometer equipped with a Globar source, Ge/KBr beam splitter, and a DTGS detector. The spectra were recorded at variable temperatures ranging from −55 to −100 °C with 100 scans at a resolution of 1.0 cm$^{-1}$. The temperature studies in the liquified noble gas were carried out in a specially designed cryostat cell, which is composed of a copper cell with a 4 cm

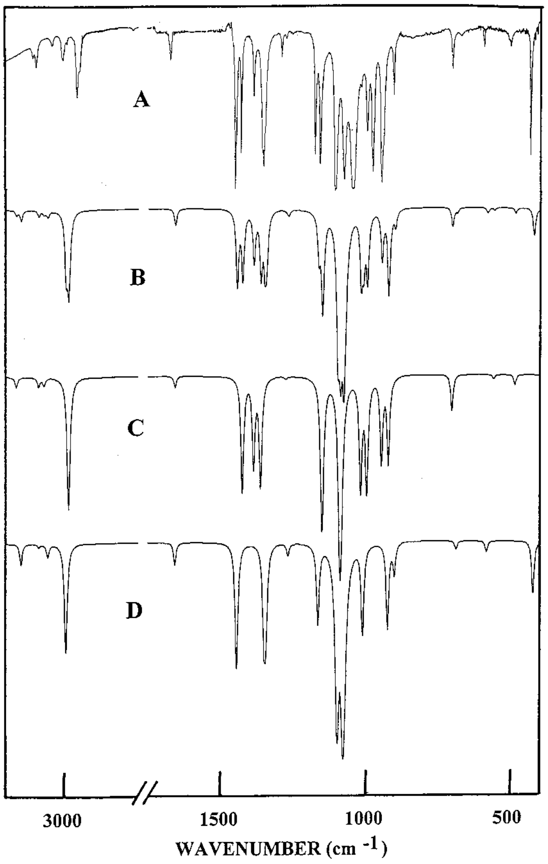

**Figure 8.** Mid-infrared spectra of 3,3-difluoropropene: (A) xenon solution at −55 °C; (B) calculated spectrum of the mixture of both conformers; (C) calculated spectrum of the gauche conformer; (D) calculated spectrum of the cis conformer.

path length and wedged silicon windows sealed to the cell with indium gaskets. The temperature is monitored by two Pt thermoresistors, and the cell is cooled by boiling liquid nitrogen. The complete cell is connected to a pressure manifold to allow for the filling and evacuation of the cell. After the cell is cooled to the desired temperature, a small amount of sample is condensed into the cell. Next, the pressure manifold and the cell are pressurized with xenon, which immediately starts condensing in the cell, allowing the compound to dissolve.

## Ab Initio Calculations

The geometry optimization of 3,3-difluoropropene was performed by the LCAO-MO−SCF restricted Hartree−Fock (RHF) calculations with the program Gaussian 94 using Gaussian-type basis sets.[20] The energy minimum with respect to the nuclear coordinates was obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay.[21] Calculations were also carried out with full electron correlation by the perturbation method[22] to second order, i.e., MP2/6-31G(d), and the determined parameters are listed in Table 1. According to these ab initio calculations, the energy difference between the cis and gauche conformers varies from a low of 2 cm$^{-1}$ to a high of 266 cm$^{-1}$ from the MP2/6-31G(d) and MP2/6-311+G(d,p) calculations, respectively, will all calculations favoring the cis conformer as the more stable rotamer.

The optimized geometry was obtained from the MP2/6-311+G(d,p) calculation for the cis conformer and then utilized to obtain a potential surface scan. In this potential surface scan, only the torsional dihedral angle was allowed to vary in 10° increments from 0° (cis) to 180° (trans). The resulting potential function indicated an additional minimum at 113° which corresponds to the gauche conformer. The surface scan is given by the dashed line in Figure 9. Optimization at the cis and gauche minima from the MP2/6-311+G(d,p) calculations gives energies of −315.774 363 and −315.771 349 hartree (1 hartree = 219 474 cm$^{-1}$), respectively, which are consistent with a more stable cis conformer and with the gauche rotamer minimum lying 266 cm$^{-1}$ higher in energy. Combined with optimization at torsional dihedral angles of 30°, 60°, 90°, 150° and 180° and using the MP2/6-311+G(d,p) basis set, this procedure leads to a more meaningful potential surface, and these data are illustrated by a solid line in Figure 9. Therefore, the theoretical cis to gauche, gauche to gauche, and gauche to cis barriers are 789, 778, and 520 cm$^{-1}$, respectively, from this basis set.

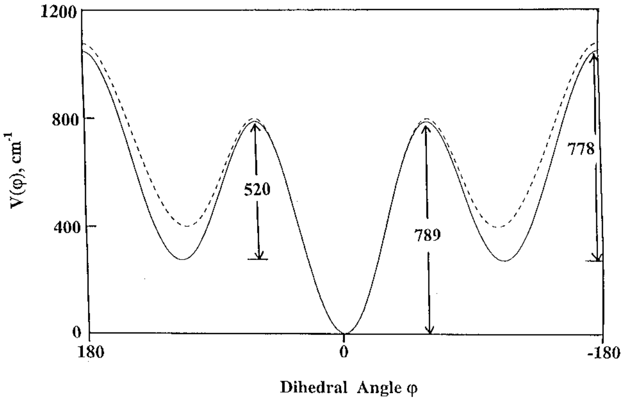

**Figure 9.** Potential function governing internal rotation of 3,3-difluoropropene as determined with the MP2/6-311+G(d,p) basis set. The potential surface given by the dashed line was obtained by allowing the torsional dihedral angle to vary by 10° increments while all other structural parameters were held fixed at the optimized value obtained for the cis conformer. The potential surface given by the solid line was calculated by allowing for optimization at the gauche to gauche and gauche to cis transition states and at the gauche minimum by relaxation of all the geometric parameters.

The intramolecular harmonic force fields were calculated with the Gaussian 94 program[20] at the RHF/6-31G(d) and MP2/6-31G(d) levels. Internal coordinates were used to form the symmetry coordinates listed in Table 2S of the Supporting Information. The Cartesian coordinates obtained for the optimized geometry were used to calculate the B-matrix elements from the G-matrix program of Schachtschneider.[23] These B-matrix elements were use to convert the ab initio force fields in Cartesian coordinates to a force field in desired internal coordinates and the resulting force constants are listed in Tables 3S and 4S of the Supporting Information. These force fields were used to reproduce the ab initio vibrational frequencies for both conformers without a scaling factor and they are given in Table 2. Scaling factor of 0.9 for all of the stretches and carbon−hydrogen bends, and 1.0 for heavy atom bends and the torsions were input along with the force field into the perturbation program to obtain the “fixed scaled” force fields, vibrational frequencies, and potential energy distributions (PED). These data are also listed in Table 2.

To aid the vibrational assignment, the theoretical infrared spectra of both the cis and gauche conformers were calculated as well as mixtures of the two conformers with various enthalpy differences between them. The infrared intensities were calculated based on the dipole moment derivatives with respect to

**TABLE 2: Observed and Calculated Frequencies ($cm^{-1}$) for 3,3-Difluoropropene**

| | | cis | | | | | | | gauche | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| vib. no. | fundamental | ab initio[a] | fixed scaled[b] | IR int.[c] | Raman act.[d] | dp ratio | obsd[e] | PED.[f] | ab initio[a] | fixed scaled[b] | IR int.[c] | Raman act.[d] | dp ratio | obsd[e] | PED.[f] |
| A′ Species | | | | | | | | | | | | | | | |
| $\nu_1$ | $=CH_2$ sym. stretch | 3316 | 3146 | 6.0 | 57.64 | 0.58 | 3104 | $42S_1,35S_3,23S_2$ | 3252 | 3086 | 2.5 | 128.53 | 0.18 | 3044 | $66S_1,23S_2,10S_3$ |
| $\nu_2$ | $=CH_2$ asym. stretch | 3253 | 3086 | 0.9 | 93.71 | 0.32 | 3054 | $50S_2,46S_1$ | 3234 | 3068 | 2.2 | 40.70 | 0.28 | 2995 | $60S_2,35S_3$ |
| $\nu_3$ | $C_3-H_4$ stretch | 3220 | 3055 | 3.7 | 86.63 | 0.12 | 3006 | $62S_3,28S_2,10S_1$ | 3333 | 3162 | 2.8 | 50.45 | 0.73 | 3108 | $54S_3,28S_1,17S_2$ |
| $\nu_4$ | $C_6-H_7$ stretch | 3155 | 2993 | 39.4 | 36.16 | 0.29 | 2966 | $100S_4$ | 3146 | 2984 | 53.2 | 101.26 | 0.28 | 2952 | $100S_4$ |
| $\nu_5$ | $C=C$ stretch | 1745 | 1656 | 6.2 | 24.25 | 0.17 | 1662 | $66S_5,14S_6$ | 1746 | 1656 | 3.1 | 26.74 | 0.19 | 1662 | $68S_5,14S_6$ |
| $\nu_6$ | $=CH_2$ scissor | 1521 | 1443 | 49.0 | 4.71 | 0.52 | 1439 | $66S_6,13S_7$ | 1501 | 1424 | 43.5 | 11.76 | 0.56 | 1421 | $69S_6,10S_9$ |
| $\nu_7$ | $C_3C_6H_7$ bend | 1414 | 1342 | 31.9 | 17.46 | 0.50 | 1347 | $40S_7,17S_6,14S_5$ | 1434 | 1361 | 40.5 | 2.52 | 0.40 | 1347 | $34S_7,22S_{15},16S_{12},15S_{20}$ |
| $\nu_8$ | $C=CH$ bend | 1336 | 1267 | 3.3 | 9.96 | 0.33 | 1283[g] | $26S_8,29S_{14},20S_{11},11S_5$ | 1344 | 1275 | 0.6 | 20.86 | 0.39 | 1288 | $34S_8,27S_{14},15S_5,15S_{11}$ |
| $\nu_9$ | $C-C$ stretch | 1227 | 1164 | 26.0 | 4.01 | 0.71 | 1176 | $36S_9,34S_8,12S_{11},11S_7$ | 995 | 947 | 29.2 | 1.41 | 0.74 | 956 | $33S_9,18S_7,15S_{12},12S_{11}$ |
| $\nu_{10}$ | $CF_2$ sym. stretch | 1156 | 1097 | 125.8 | 4.01 | 0.35 | 1105 | $67S_{10},11S_{13}$ | 1213 | 1151 | 71.2 | 1.90 | 0.75 | 1156 | $23S_{10},24S_{16},12S_9,10S_8$ |
| $\nu_{11}$ | $=CH_2$ wag | 949 | 901 | 8.6 | 4.19 | 0.14 | 911 | $54S_{11},19S_9$ | 1037 | 998 | 43.3 | 4.69 | 0.75 | 988 | $44S_{11},24S_{16},19S_8$ |
| $\nu_{12}$ | $CF_2$ scissor | 614 | 583 | 3.1 | 2.07 | 0.10 | 606 | $20S_{12},27S_{13},22S_{10},11S_9$ | 393 | 375 | 7.5 | 5.65 | 0.67 | (383) | $22S_{12},15S_{19},14S_{13},10S_7$ |
| $\nu_{13}$ | $CF_2$ wag | 445 | 422 | 15.7 | 2.19 | 0.45 | 444 | $62S_{13},19S_{12},12S_9$ | 513 | 487 | 2.8 | 1.49 | 0.72 | 518 | $73S_{13}$ |
| $\nu_{14}$ | $C=CC$ in-plane bend | 341 | 323 | 6.5 | 2.07 | 0.61 | 338 | $50S_{14},25S_8,10S_7,10S_{12}$ | 587 | 560 | 1.3 | 4.95 | 0.66 | 566 | $22S_{14},18S_{20},17S_{19}$ |
| A″ Species | | | | | | | | | | | | | | | |
| $\nu_{15}$ | $C_6H_7$ bend | 1420 | 1348 | 30.7 | 4.50 | 0.75 | 1354 | $65S_{15},34S_{20}$ | 1460 | 1385 | 30.5 | 5.11 | 0.71 | 1376 | $42S_{15},19S_7,17S_{20}$ |
| $\nu_{16}$ | $CF_2$ asym. stretch | 1134 | 1077 | 208.7 | 4.54 | 0.75 | 1061 | $90S_{16}$ | 1145 | 1088 | 151.9 | 4.06 | 0.59 | (1089) | $43S_{16},34S_{10}$ |
| $\nu_{17}$ | $=CH_2$ rock | 1029 | 1011 | 30.6 | 2.15 | 0.75 | 1006 | $67S_{17},30S_{19}$ | 1052 | 1019 | 42.4 | 2.50 | 0.63 | 1023 | $69S_{17},26S_{19}$ |
| $\nu_{18}$ | $C=CH$ bend | 973 | 924 | 28.8 | 0.87 | 0.75 | 948 | $99S_{18}$ | 973 | 923 | 29.4 | 5.11 | 0.16 | 946 | $98S_{18}$ |
| $\nu_{19}$ | $=CH$ twist | 714 | 688 | 2.3 | 4.81 | 0.75 | 683 | $45S_{19},23S_{17},16S_{20}$ | 738 | 704 | 10.4 | 4.64 | 0.38 | 712 | $22S_{19},19S_9,19S_{10},19S_{12}$ |
| $\nu_{20}$ | $CF_2$ twist | 325 | 310 | 0.6 | 6.78 | 0.75 | 323 | $44S_{20},28S_{15},17S_{19}$ | 284 | 270 | 0.5 | 1.24 | 0.67 | 274 | $26S_{20},31S_{14},22S_{15},17S_8$ |
| $\nu_{21}$ | $CHF_2$ torsion | 100 | 100 | 0.4 | 8.79 | 0.75 | 93 | $91S_{21}$ | 106 | 106 | 0.6 | 9.08 | 0.75 | 98 | $91S_{21}$ |

[a] Calculated values are obtained by ab initio calculations with the MP2/6-31G* basis set. [b] Calculated using scaling factors of 0.9 for CH stretches and 1.0 for all heavy atom bends and torsions. [c] Infrared intensities are in km/mol. [d] Calculated Raman activities in Å$^4$/amu. [e] Frequencies are from the infrared spectrum of the gas and xenon solutions except those in parentheses from the Raman spectrum of the gas. [f] Potential energy distribution predicted by ab initio calculations. [g] Frequencies are from the Raman spectrum of the solid.

the Cartesian coordinates. The derivatives were taken from the ab initio calculations transformed to normal coordinates by

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

where $Q_i$ is the $i$th normal coordinate, $X_j$ is the $j$th Cartesian displacement coordinate, and $L_{ij}$ is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by

$$I_i = \frac{N\pi}{3c^2}\left[\left(\frac{\partial\mu_x}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_y}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_z}{\partial Q_i}\right)^2\right]$$

In Figure 8D, the predicted infrared spectrum of the more stable cis conformer is shown and in Figure 8C that for the gauche conformer. The predicted infrared spectrum of the mixture is shown in Figure 8B with the enthalpy difference of 82 $cm^{-1}$ (value from xenon solution) with the cis conformer the more stable rotamer. The experimental infrared spectrum of 3,3-difluoropropene dissolved in liquid xenon at −55 °C is also shown for comparison in Figure 8A. The agreement between the observed and calculated infrared spectra is excellent and these data were quite valuable for supporting the vibrational assignment.

The Raman spectra have also been predicted from the ab initio calculations. The evaluation of Raman activity by using the analytical gradient method has been developed.[24,25] 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 $j$, $\alpha_j$ is the derivative of the isotropic polarizability, and $\beta_j$ is that of the anisotropic polarizability. The Raman scattering cross sections, $\partial\sigma_j/\partial\Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activities and the predicted wavenumbers for each normal mode using the relationship[26,27]

$$\frac{\partial\sigma_j}{\partial\Omega} = \left(\frac{2^4\pi^4}{45}\right)\left(\frac{(\nu_0-\nu_j)^4}{1-\exp\left[\frac{-hc\nu_j}{kT}\right]}\right)\left(\frac{h}{8\pi^2 c\nu_j}\right)S_j$$

where $\nu_0$ is the exciting wavenumber, $\nu_j$ is the vibrational wavenumber of the $j$th normal mode, and $S_j$ is the corresponding Raman scattering activity. To obtain the polarized Raman scattering cross sections, the polarizabilities are incorporated into $S_j$ by $S_j[(1 - \rho_j)/(1 + \rho_j)]$ where $\rho_j$ is the depolarization ratio of the $j$th normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the standard Gaussian program were used together with a Lorentzian function to obtain the calculated spectra.

The predicted Raman spectra of the pure cis and gauche conformers are shown in parts D and C of Figure 10,

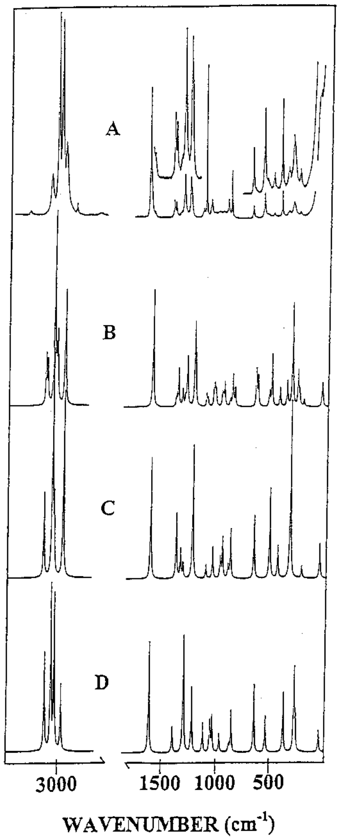

**Figure 10.** Raman spectra of 3,3-difluoropropene: (A) liquid; (B) calculated spectrum of the mixture of both conformers; (C) calculated spectrum of the gauche conformer; (D) calculated spectrum of the cis conformer.

respectively. In Figure 10B the mixture of the two conformers is shown with the experimentally determined $\Delta H$ value of 82 cm$^{-1}$ with the cis conformer the more stable form. The experimental Raman spectrum of the liquid is shown in Figure 10A for comparison and the agreement is considered satisfactory, although there are some significant differences particularly in the low-frequency spectral region.

## Conformational Stability

A comparison of the Raman spectrum of the gas with that of the solid, indicates that the Raman lines observed in the spectrum of the gas at 1427, 1382, 1296, 944, 715, 569, 516, and 273 cm$^{-1}$ which correspond to the Raman lines in the liquid at 1425, 1380, 1293, 944, 712, 576, 516, and 278 cm$^{-1}$ disappear from the spectrum of the annealed solid. Other lines were also observed in the Raman spectrum of the gas at 1358, 1089, 955, and 383 cm$^{-1}$ with no corresponding lines in the liquid, which are also absent upon crystallization. These observations clearly indicate the presence of two conformers in the fluid phases. The disappearance of the Raman lines in the liquid at 712, 516, and 278 cm$^{-1}$ is especially important in identifying the cis form as the conformer remaining in the solid since only the gauche conformer is predicted from ab initio calculations to have fundamental modes in this spectral region. Therefore, all of the Raman lines persisting in the spectrum of the solid are attributed to the cis conformer which indicates that this rotamer is the stable form in the solid phase.

To gain information about the enthalpy difference between the two conformers similar to what is expected for the gas, a variable temperature study in liquified xenon was carried out. The sample was dissolved in liquified xenon, and the spectra were recorded at different temperatures varying from −55 to −100 °C. Only small interactions are expected to occur between the dissolved sample and the surrounding xenon atoms and, consequently, only small frequency shifts are anticipated when passing from the gas phase to the liquified noble gas solutions.[28−32] A significant advantage of this temperature study is that the conformer bands are better resolved in comparison with those in the infrared spectrum of the gas (Figure 3). This is particularly important since most of the conformer bands for this molecule are predicted to be observed within a few wavenumbers of each other. Also the areas of the conformer peaks are more accurately determined than those from the spectrum of the gas.

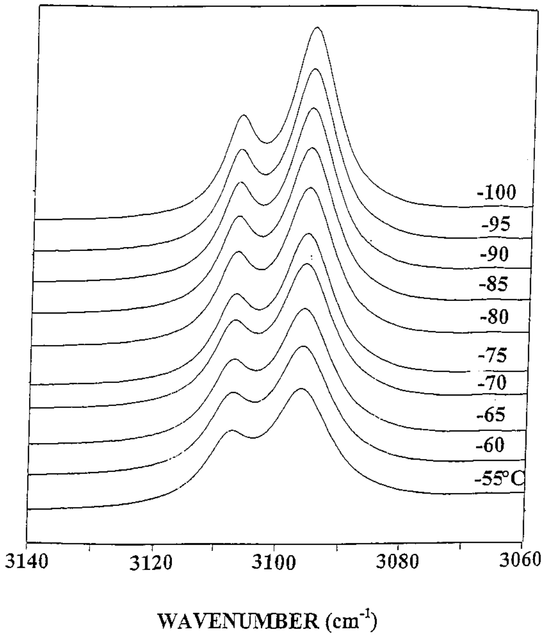

**Figure 11.** Temperature dependence of infrared spectra in the region of 3140 to 3060 cm$^{-1}$ of 3,3-difluoropropene in xenon solution.

The bands used for the conformational stability studies from the infrared spectrum of the xenon solution are those assigned to the =C−H stretch at 3108 cm$^{-1}$ (gauche), =CH$_2$ symmetric stretch at 3097 cm$^{-1}$ (cis), and =CH$_2$ twist at 712 cm$^{-1}$ (gauche) along with CF$_2$ wag at 444 cm$^{-1}$ (cis). In all, 10 sets of spectral data were obtained for these two pairs of conformer bands (Figures 11 and 12). The intensities of the infrared bands were measured as a function of temperature, and their ratios were determined. By application of the van't Hoff equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where $\Delta S$ is the entropy change, $\Delta H$ was determined from a plot of $-\ln K$ versus $1/T$, where $\Delta H/R$ is the slope of the line and $K$ is the appropriate intensity ratio. It is assumed that $\Delta H$ is not a function of temperature.

From a plot of the natural logarithm of the ratio, $I_{3097}/I_{3108}$, as a function of the reciprocal of the absolute temperature, the $\Delta H$ value is determined to be 89 ± 12 cm$^{-1}$ with the cis form the more stable rotamer. Similarly, the pair at 712 (gauche) and 444 (cis) gives a $\Delta H$ value of 74 ± 8 cm$^{-1}$ again with the cis conformer the more stable form (Table 3). The average of these two values is 82 ± 10 cm$^{-1}$ where the error limits are given by the standard statistical deviation of the measured areas of the intensity data. These error limits do not take into account small associations with the liquid xenon or other experimental factors such as the presence of overtones or combination bands in near coincidence with the measured areas of the fundamentals.

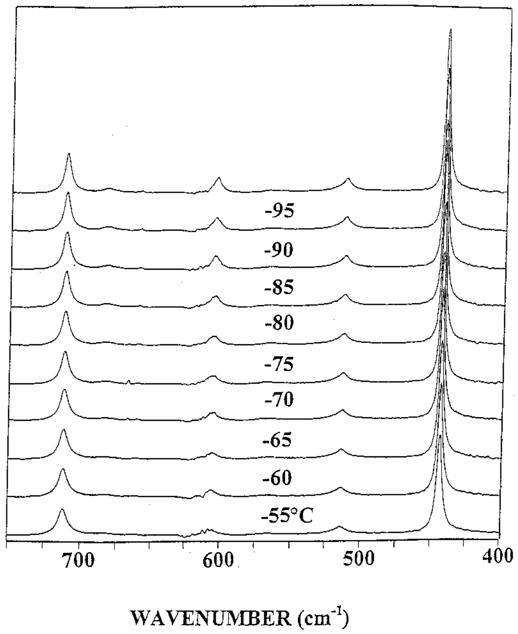

**Figure 12.** Temperature dependence of infrared spectra in the region of 750 to 400 cm$^{-1}$ of 3,3-difluoropropene in xenon solution.

**TABLE 3: Temperature and Intensity Ratios from Conformational Study of 3,3-Difluoropropene**

| $T$ (°C) | 1000/$T$ (K) | $I_{444}/I_{712}$ | $I_{3097}/I_{3108}$ |
|---|---|---|---|
| −55 | 4.58 | 2.620 | 2.381 |
| −60 | 4.69 | 2.634 | 2.487 |
| −65 | 4.80 | 2.668 | 2.524 |
| −70 | 4.92 | 2.671 | 2.527 |
| −75 | 5.05 | 2.825 | 2.539 |
| −80 | 5.18 | 2.810 | 2.602 |
| −85 | 5.31 | 2.876 | 2.667 |
| −90 | 5.46 | 2.873 | 2.676 |
| −95 | 5.61 | 2.907 | 2.878 |
| −100 | 5.78 | 2.951 | 2.753 |
| $\Delta H$[a] (cm$^{-1}$) | | 74 ± 8 | 89 ± 12 |

[a] Average value of $\Delta H$ is 82 ± 10 cm$^{-1}$ (0.98 ± 0.12 kJ/mol), with the cis conformer being the more stable form.

## Vibrational Assignment

Since there are no previous vibrational assignments proposed for this molecule, the current Raman and infrared spectra have been used to provide a complete assignment for the normal modes for the cis conformer. All bands, which are observed in the fluid phases but disappeared in the crystal, have been assigned to the gauche conformer. The assignment was assisted by the wavenumbers predicted from the ab initio calculations along with relative intensities and infrared band contours. The assignments made for the fundamentals associated with the carbon−hydrogen modes should be considered tentative in the absence of selective deuteration studies. These assignments are summarized in Table 2.

The cis conformer of 3,3-difluoropropene has $C_s$ symmetry and the fundamental vibrations span the irreducible representations, 14 A′ + 7A″. From a reasonable set of structural parameters (Table 1) it is shown that the *b* principal axis is perpendicular to the symmetry plane for the cis conformer. Therefore, the out-of-plane modes are expected to give rise to B-type infrared band contours and the in-plane modes should be A-, C-, or A/C-hybrid type contours (Figure 13). The gauche form has $C_1$ symmetry and gives rise to A-, B-, C− or any hybrid-type infrared band contour.

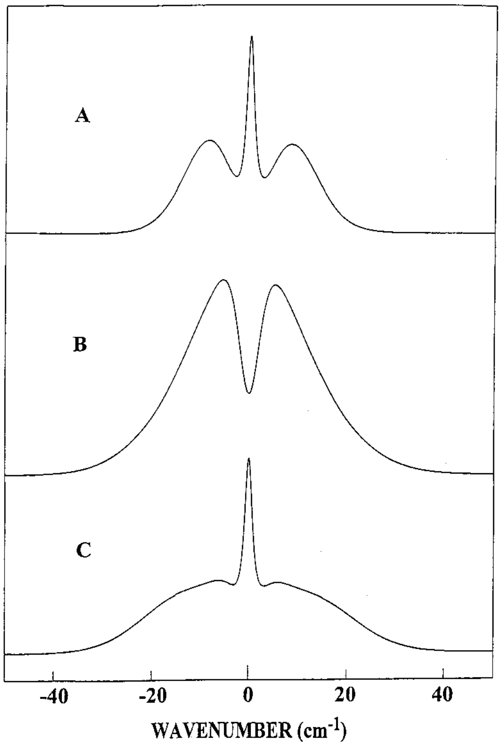

**Figure 13.** Predicted infrared band contour of *cis*-3,3-difluoropropene: (A) pure A-type; (B) pure B-type; (C) pure C-type.

**Carbon−Hydrogen Modes.** For the cis conformer, all four carbon hydrogen stretching modes belong to the A′ species. In the Raman spectrum of the gas, four pronounced lines are observed at 3104, 3053, 3016, and 2966 cm$^{-1}$, which are also present in the spectrum of the solid can readily be assigned to these four A′ modes in the decreasing wavenumber order for the $=CH_2$ symmetric and antisymmetric stretches, $=C-H$ stretch and $C_6-H_7$ stretch, respectively, as predicted from the ab initio calculations. Three additional lines appear at 3116, 3007, and 2959 cm$^{-1}$, which disappeared from the Raman spectrum of the annealed solid and they have been assigned as the corresponding modes for the gauche conformer.

The assignments of the $=CH_2$ bending modes are consistent with those of corresponding modes for similar molecules.[1−8] Between 1500 and 1300 cm$^{-1}$ we observed two A-type bands at 1444 and 1426 cm$^{-1}$, a C-type band at 1382 cm$^{-1}$, and three Q-branches at 1361, 1347, and 1343 cm$^{-1}$ in the infrared spectrum of the gas. The corresponding Raman lines in the spectrum of the gas are observed at 1445, 1427, 1382, 1358, 1348, and 1338 cm$^{-1}$, in which three of them (1444, 1347, and 1336 cm$^{-1}$) remain in the Raman spectrum of the annealed solid. These three bands have been assigned as the $=CH_2$ scissors and the in- and out-of-plane (A″) $C_3C_6H_7$ bends for the cis conformer, respectively, whereas the remaining bands are assigned the corresponding modes for the gauche form. The B-type band observed at 1006 cm$^{-1}$ and the sharp Q transition at 915 cm$^{-1}$ have been assigned as the $=CH_2$ rock and $=CH_2$ wag, respectively, as the frequency order and band contours are in good agreement with the predictions from the ab initio calculations. The weak line at 695 cm$^{-1}$ in the Raman spectrum of the solid was not observed in the Raman spectrum of the gas. Therefore, this transition should be a mode of A″ symmetry and it has been assigned as the $=CH_2$ twist.

The assignments of the $C=C-H$ bending modes are consistent with those given previously for the corresponding modes in similar molecules.[1−8] In the studies of 3-fluoropropene, the

**TABLE 4: Observed and Assigned Asymmetric Torsional Transitions of 3,3-Difluoropropene**

| transition | obsd (cm$^{-1}$) | calcd (cm$^{-1}$)$^a$ | $\Delta^b$ |
|---|---|---|---|
| | | cis | |
| 1 ← 0 | 92.58 | 91.91 | 0.67 |
| 2 ← 0 | 179.65 | 180.80 | −1.15 |
| 3 ← 1 | 173.75 | 174.27 | −0.52 |
| 4 ← 2 | 166.99 | 166.67 | 0.32 |
| 5 ← 3 | 156.97 | 157.64 | −0.67 |
| 6 ← 4 | 147.22 | 146.37 | 0.85 |
| | | gauche | |
| 1∓ ← 0± | 97.65 | 98.01 | −0.36 |
| 2± ← 1∓ | 93.46 | 93.33 | 0.13 |
| 3∓ ← 2± | 89.04 | 88.24 | 0.81 |
| 4± ← 3∓ | 81.86 | 82.48 | −0.62 |
| 5∓ ← 4± | 75.95 | 75.32 | 0.63 |

[a] Calculated using $F_0 = 1.759098$, $F_1 = -0.099929$, $F_2 = 0.031564$, $F_3 = 0.004673$, $F_4 = 0.004440$, $F_5 = -0.000373$, $F_6 = -0.000188$, $F_7 = -0.000022$, $F_8 = 0.000008$ and the potential parameter values listed in Table 5. [b] obsd − calcd.

C═C−H in-plane and out-of-plane bends are assigned[5] to the bands at 1292 and 996 cm$^{-1}$ in the infrared spectrum of the gas, respectively. For 3,3-difluoropropene, the corresponding modes for the cis conformer have been assigned to the bands at 1286 and 948 cm$^{-1}$ in the infrared spectrum of the xenon solution.

**Skeletal Modes.** On the basis of the prediction of infrared band contours (Figure 13), the C═C−C in-plane bend should be mainly a C-type band around 323 cm$^{-1}$. In the infrared spectrum of the gas (Figure 5), a typical C-type band at 338 cm$^{-1}$ was observed, which remained in the infrared and Raman spectra of the annealed solid. Therefore, we assigned this band to the C═C−C in-plane bending mode for the cis conformer. For the C(H)F$_2$ group, there are bands at 608, 444, and 323 cm$^{-1}$ in the infrared spectrum and these bands are due to the CF$_2$ scissor, wag, and twist, respectively, of the cis conformer with the assignments in agreement with those given previously for the corresponding modes in difluoromethylcyclopropane.[18]

**Asymmetric Torsion.** The far-infrared spectra of gaseous 3,3-difluoropropene in different spectral regions are shown in Figures 5−7. In the region of the asymmetric torsion (Figure 6), a series of well-defined Q-branches are observed at 97.65, 93.46, 89.04, and 81.86 cm$^{-1}$. The asymmetric torsion of one of the conformers must be due to this series of four pronounced Q-branches with the fundamental at 97.6 cm$^{-1}$ with successive "hot bands" falling to lower frequency. Since the A″ modes of the cis conformer give rise to B-type bands these Q-branches must be due to the gauche conformer. Also, a number of sharp bands are observed in the far-infrared spectrum of the gas between 180 and 140 cm$^{-1}$ as shown in Figure 7. Of these, the Q-branches at 179.65, 173.75, 166.99, 156.97, and 147.22 occur in the region in which one expects to observe the two-quantum transitions of the asymmetric torsion of one of the conformers. The assignment of these Q-branches is given in Table 4, and the frequency for the first observed transition in the higher wavenumber series is too low for the overtone of the Q-branches at 97.65 and 93.46 cm$^{-1}$. Therefore, these overtones must be due to the torsional mode of the other conformer, i.e., the cis rotamer.

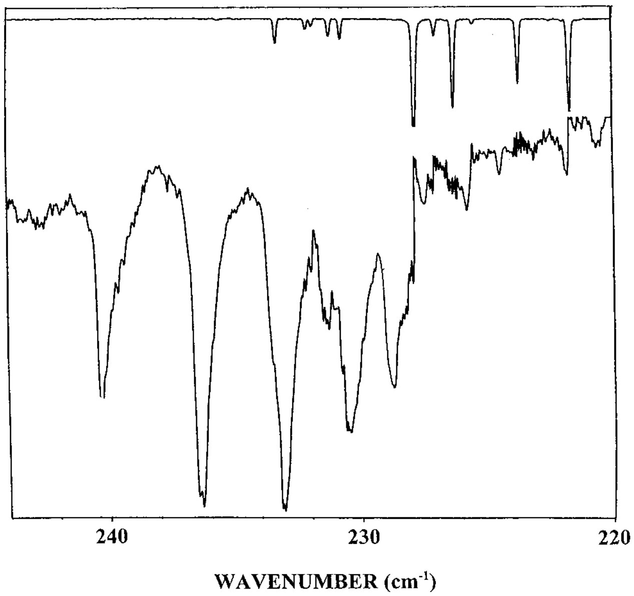

**Figure 14.** Far infrared spectrum of 3,3-difluoropropene in the region of 244 to 220 cm$^{-1}$ in the gas.

In the region of 244 to 220 cm$^{-1}$, a series of weak Q-branches has been observed at 228.74, 230.45, 233.16, 236.36, and 240.35 cm$^{-1}$ (Figure 14). According to the ab initio predictions, there are no fundamental modes in this spectral region and, therefore, these bands must belong to overtone and/or combination or difference bands. For the cis conformer, the CF$_2$ twist (A″) has been assigned at 323 cm$^{-1}$, and if the 230 cm$^{-1}$ is a difference band then the asymmetric torsion should be about 93 cm$^{-1}$, which is consistent with the overtone assignments for the torsional mode of the cis form.

With the torsional transition assignments, the potential function governing the conformational interchange has been calculated. The torsional dihedral angular dependence of the internal rotation constant, $F(\phi)$, can be represented as a Fourier series:

$$F(\phi) = F_0 + \sum_{i=1}^{6} F_i \cos i\phi$$

The relaxation of the structural parameters, $B(\phi)$, during the internal rotation can be incorporated into the above equation by assuming that they are small periodic functions of the torsional angle of the general type

$$B(\phi) = a + b \cos \phi + c \sin \phi$$

The structural parameters (Table 1) obtained from the optimized geometries for both the cis and gauche conformers, utilizing the adjusted structural parameters, were used to obtain the kinetic constants.

The torsional potential is also represented as a Fourier cosine series in the internal angle ($\phi$),

$$V(\phi) = \sum_{i=1}^{6} \left(\frac{V_i}{2}\right)(1 - \cos i\phi)$$

The kinetic terms, the asymmetric torsional frequencies for both conformers, the experimental enthalpy, and the gauche dihedral angle were used to fit the potential function utilizing a program[33] written in our laboratory.

In the initial calculation of the potential parameters the transition assigned as the 1 ← 0 for the cis and ±1 ← ∓0 transition for the gauche (Table 4) were used along with the value of 82 cm$^{-1}$ for $\Delta H$ and a dihedral angle of 113.0° for the gauche rotamer. As the values for the potential parameters converged, three more transitions for the gauche rotamer as well as four two quantum transitions for the cis conformer were added

**TABLE 5: Potential Function Parameter Values ($cm^{-1}$) for the Asymmetric Torsion of 3,3-Difluoropropene and Barriers to Interconversion ($cm^{-1}$)**

| potential constants | experimental value | ab initio MP2/6-311+G(d,p) | $C_3H_5CHF_2$ value[a] |
|---|---|---|---|
| $V_1$ | 215 ± 16 | 372 | 229 ± 5 |
| $V_2$ | −111 ± 17 | −41 | 40 ± 4 |
| $V_3$ | 633 ± 6 | 683 | 1270 ± 3 |
| $V_4$ | 54 ± 8 | 60 | −136 ± 2 |
| $V_5$ | −25 ± 4 | −7 | - |
| $V_6$ | −12 ± 2 | −12 | - |
| $\Delta H$ ($cm^{-1}$) | 82 ± 39 | 269 | 102 ± 8 |
| gauche/cis barrier | 560 | 520 | 1155 |
| cis/gauche barrier | 639 | 789 | 1255 |
| gauche/gauche barrier | 744 | 778 | 1399 |
| dihedral angle | 113.0 ± 0.1 | 113.0 | 121.6 |

[a] Reference 18.

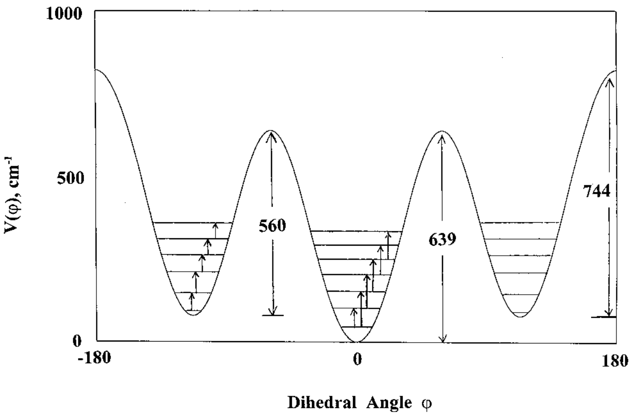

**Figure 15.** Asymmetric torsional potential function for 3,3-difluoropropene as determined from far infrared spectral data. The torsional dihedral angle of 0° corresponds to the cis conformer.

to the calculation. The final resulting values for the potential parameters are listed in Table 5, and the potential function is shown in Figure 15.

## Discussion

From the study of the vibrational spectra of gaseous, liquid, and solid 3,3-difluoropropene, the cis conformer has been identified as the stable form in all three physical states, which is similar to what was found for the difluoromethylcyclopropane. This is the conformer one would expect to be more stable on the basis of the relatively weak steric interaction of the hydrogen atom with the double bond. All the ab initio calculations predict the cis conformer to be the more stable form, which is consistent with the experimental enthalpy value of 82 ± 10 $cm^{-1}$ (0.98 ± 0.12 kJ/mol) from the variable temperature study in xenon solution. This experimental value of $\Delta H$ is expected to be similar to the value for the gas since the dipole moment of the two conformers are predicted to have similar values and the molecular sizes of the two rotamers are nearly the same.[28−32] However, the energy difference is predicted to be from 2 $cm^{-1}$ from the MP2/6-31G(d) calculation to 266 $cm^{-1}$ from the MP2/6-311+G(d,p) calculation.

In the previously reported microwave study[34] of 3,3-difluoropropene, using relative intensity measurements it was concluded that the cis conformer is more stable than the gauche form by 260 ± 80 $cm^{-1}$, which is significantly higher than the value of 82 ± 10 $cm^{-1}$ obtained in the present study. It is probably that the microwave value has a much larger uncertainty than the quoted value since the measurement of relative intensities in microwave spectroscopy is quite difficult. Corresponding three-member ring molecules are frequently compared to the corresponding ethylenic molecules, so a comparison of similar results obtained for difluoromethylcyclopropane[18] seems appropriate. We have previously reported the enthalpy value for the difluoromethylcyclopropane from xenon solution to be 102 ± 8 $cm^{-1}$ with the cis conformer the more stable rotamer (Table 5). Therefore, this value is comparable to the enthalpy difference of 82 ± 10 $cm^{-1}$ for 3,3-difluoropropene, which was also obtained from xenon solutions. However, for difluoromethylcyclopropane, the ab initio calculations predict the gauche conformer to be the more stable form but by only 15 $cm^{-1}$ from the MP2/6-311+G(2d,2p) calculation with the smaller basis set of MP2/6-311+G(d,p), the gauche conformer is predicted to be the more stable rotamer for difluoromethylcyclopropane. Therefore, it would be of interest to determine what size basis set was needed to correctly predict the stability of this corresponding three-membered ring.

The predicted structural parameters from the MP2/6-311+G(d,p) and MP2/6-311+G(2d,2p) calculations are very similar for the two conformers except for the CC and CF bond distances. The CC bond distance is predicted to be 0.007 Å longer for the gauche conformer, whereas one of the CF distances is longer while the other one is shorter than the CF distance in the cis rotamer. The C=C−C angle opens about 1.8° when one of the fluorine atoms (gauche) is eclipsing the double bond. These differences are consistent with those predicted for the corresponding parameters for difluoromethylcyclopropane.

Utilizing a new computer program developed in this laboratory, which combines[5] the ab initio predicted parameters and microwave previously reported[34] rotational constants we have obtained reasonable $r_o$ structural parameters. We utilized the ab initio parameters from the MP2/6-311+G(d,p) calculation since this basis set gives carbon−hydrogen distances similar to those obtained for $r_o$ parameters for allyl fluoride.[5] By using the six rotational constants for the two conformers and keeping the differences of the parameters between the two conformers the same as the predicted ab initio values the “adjusted $r_o$” parameters were obtained. All the carbon−hydrogen distances formed one set and the carbon−hydrogen angles another set. The three heavy atom distances and the CCC angle were each treated as separate sets. As shown in Table 1, all of the adjusted $r_o$ parameters are close to those predicted from the ab initio MP2/6-311+G(d,p) calculations with the major difference in the CC bond distance of the cis conformer. Nevertheless, it is believed that these determined parameters should be within 0.005 Å of the actual distances and about 1° for the angles. However, there is a large difference between the experimental dipole moment values and those predicted from the ab initio calculations, which is normally found for predicted dipole moment values.

Because of the similarity of the structure parameters for the two conformers one might expect the force constants to be very similar for the two rotamers. However, there are some significant differences, which should be noted. Although the C−C distance for the gauche conformer is predicted to be at least 0.006 Å longer than that for the cis conformer, the stretching force constant for this bond is only slightly smaller for the gauche conformer than the corresponding force constant for the cis rotamer. The major difference is for the C=C−H bending force constant, when one of the fluorine atoms eclipses the double bond which increases the force constant ($\theta$) from 0.339 to 0.373 mdyn/Å. Also, the bending force constant for the C=C−C angle increases by about 20% for the gauche conformer and the bending force constant for the C−C−F angle increases by about

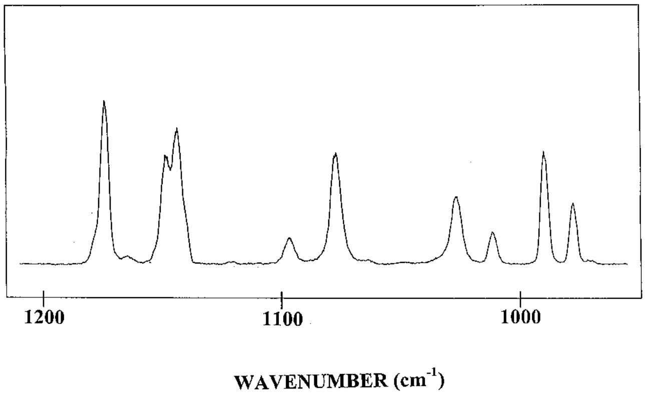

**Figure 16.** Raman spectrum of 3,3-difluoropropane in the region of 1210 to 960 $cm^{-1}$ in the annealed solid.

40%. These changes in the bending force constants result in large difference in the frequencies of the bending modes. For example, the C═C−C in-plane bend is assigned at 346 $cm^{-1}$ for the cis conformer but it is at 566 $cm^{-1}$ for the gauche form. Similarly, the $CF_2$ deformation shifts from 444 $cm^{-1}$ for the cis conformer to 516 $cm^{-1}$ for the gauche rotamer. For this reason, the bending modes are much more indicative of the presence of conformers for these types of molecules than the stretching modes.

For the cis conformer, the PED values for the primary contributions for the A″ modes are usually greater than 50% except for the $═CH_2$ and $CF_2$ twists, which have relatively large contributions from two other symmetry coordinates. However, for the A′ symmetry species, the mixing is extensive with some vibrations having no contribution of more than 30% from any one symmetry coordinate, e.g., $\nu_8$ and $\nu_{12}$. As expected, the mixing is even more extensive for several of the modes in the gauche conformer since it has no symmetry. Therefore, the approximate descriptions of the fundamentals are simplified expression with many having the major contributions from that particular symmetry coordinate, but there are some that are given more for bookkeeping than for describing the molecular motions.

The potential coefficients obtained from the torsional transitions, the enthalpy difference from the xenon solution, and the gauche dihedral angle have statistical uncertainties (Table 5), which only reflect the fit of the torsional frequencies and not the uncertainty of the value of the enthalpy which would mainly effect the $V_1$ term. For comparison purposes, we have obtained the potential coefficients of the torsional motion from the MP2/6-311+G(d,p) calculation and they are also listed in Table 5. The $V_1$ term will be different since the ab initio calculation predicts the cis conformer to be more stable by 269 $cm^{-1}$ rather than 82 $cm^{-1}$ as determined experimentally from the xenon solution. Nevertheless, the $V_3$ term, which is essentially the barrier to conformer interchanges, is nearly the same ($V_3 = 683$ $cm^{-1}$) versus $633 \pm 6$ $cm^{-1}$ value obtained from the far-infrared data. The gauche to gauche and the cis to gauche barriers are predicted to be 778 and 520 $cm^{-1}$, respectively, which agree well with those determined from the experimental data of 744 and 560 $cm^{-1}$, respectively. From the previously reported microwave study,[34] the potential function parameters of $V_1$ and $V_3$ were determined to be $266 \pm 40$ and $508 \pm 20$ $cm^{-1}$, where the $V_1$ value is consistent with that obtained in the present study but the $V_3$ term is significantly smaller than the currently determined value.

Although we used a single scaling factor of 0.9 with the MP2/6-31G(d) calculations, the predicted frequencies are in excellent agreement with the observed values. Excluding those for the four carbon−hydrogen stretches, the average errors in the frequency predictions for the normal modes are 12 and 10 $cm^{-1}$ for the cis and the gauche conformer, respectively. Thus, in the present study, multiple scaling factors are not warranted for aiding in the vibrational assignments for the fundamental modes.

On the basis of the prediction of the ab initio calculations, there should be two fundamentals in the region of 1100 to 1000 $cm^{-1}$, the $CF_2$ symmetric and antisymmetric stretches. However, we observed four pronounced bands in the Raman spectrum of the solid (Figure 16) in this region. We believe these “extra” lines are due to factor group splitting where there are at least two molecules per unit cell. Additional support for this interpretation is found from the $═CH_2$ rock and the C−C and C═C stretches each of which gives rise to two lines in the Raman spectrum of the solid. The splitting is consistent with the limited number of lattice modes observed in both the low-frequency infrared and Raman spectra.

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**Supporting Information Available:** Table 1S, observed infrared and Raman wavenumbers ($cm^{-1}$) for 3,3-difluoropropene; Table 2S, symmetry coordinates for 3,3-difluoropropene; Table 3S, force constants in internal coordinates for cis 3,3-difluoropropene; Table 4S, force constants in internal coordinates for gauche 3,3-difluoropropene. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Durig, J. R.; Zhen, M.; Little, T. S. *J. Chem. Phys.* **1984**, *81*, 4259.

(2) Durig, J. R.; Zhen, M.; Heusel, H. L.; Joseph, P. J.; Groner, P.; Little, T. S. *J. Phys. Chem.* **1985**, *89*, 2877.

(3) Durig, J. R.; Geyer, T. J.; Little, T. S.; Durig, D. T. *J. Mol. Struct.* **1988**, *172*, 165.

(4) van der Veken, B. J.; Herrebout, W. A.; Durig, D. T.; Zhao, W.; Durig, J. R. *J. Phys. Chem.* **1999**, *103*, 3A, 1976.

(5) Durig, J. R.; Durig, D. T.; van der Veken, B. J.; Herebout, W. A. *J. Phys. Chem. A*, in press.

(6) Durig, J. R.; Jalilian, M. R. *J. Phys. Chem.* **1980**, *84*, 3543.

(7) Durig, J. R.; Tang, Q.; Little, T. S. *J. Mol. Struct.* **1992**, *269*, 257.

(8) Durig, J. R.; Tang, Q.; Little, T. S. *J. Raman Spectrosc.* **1992**, *23*, 653.

(9) Durig, J. R.; Godbey, S. E.; Faust, S. A. *J. Mol. Struct.* **1988**, *176*, 123.

(10) Kalasinsky, V. F.; Wurrey, C. J. *J. Raman Spectrosc.* **1980**, *9*, 315.

(11) Fujiwara, F. G.; Chang, J. C.; Kim, H. *J. Mol. Spectrosc.* **1977**, *41*, 177.

(12) Mohammadi, M. A.; Brooks, W. V. F. *J. Mol. Spectrosc.* **1979**, *77*, 42.

(13) Wurrey, C. J.; Kirshnamoorthi, R.; Pechsiri, S.; Kalasinsky, V. F. *J. Raman Spectrosc.* **1982**, *12*, 95.

(14) Wurrey, C. J.; Yeh, Y. Y.; Weakley, M. D.; Kalasinsky, V. F. *J. Raman Spectrosc.* **1984**, *15*, 179.

(15) Durig, J. R.; Shen, S.; Zhu, X.; Wurrey, C. J. *J. Mol. Struct.* **1999**, in press.

(16) Saebo, S.; Kavana, K. *J. Mol. Struct.* **1991**, *235*, 447.

(17) Whitehead, K. G. M.S. Thesis, Mississippi State University, 1985.

(18) Guirgis, G. A.; Little, T. S.; Lee, M. J.; Zhen, M.; Yu, Z.; Durig, J. R. *J. Phys. Chem.* **1998**, *102A*, 10460.

(19) Furic, K.; Durig, J. R. *Appl. Spectrosc.* **1988**, *42*, 175.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.3; Gaussian Inc.: Pittsburgh, PA, 1995.

(21) Pulay, P. *Mol. Phys*. **1969**, *17*, 197.
(22) Moller, C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 618.
(23) Schachtschneider, J. H. In *Vibrational Analysis of Polyatomic Molecules*; Technical Reports 231 and 57; Shell Development Co.: Houston, TX, 1964, 1965; Parts V and VI.
(24) Frisch, M. J.; Yamaguchi, Y.; Gaw, J. F.; Schaefer, H. F., III; Binkley, J. S. *J. Chem. Phys*. **1986**, *84*, 531.
(25) Amos, R. D. *Chem. Phys. Lett*. **1986**, *124*, 376.
(26) Polavarapu, P. L. *J. Phys. Chem*. **1990**, *94*, 8106.
(27) Chantry, G. W. In *The Raman Effect*; Anderson, A., Ed.; Marcel Dekker, Inc.: New York, 1971; Vol. 1, Chapter 2.
(28) Herrebout, W. A.; van der Veken, B. J. *J. Phys. Chem*. **1996**, *100*, 9671.
(29) Herrebout, W. A.; van der Veken, B. J.; Wang, A.; Durig, J. R. *J. Phys. Chem*. **1995**, *99*, 578.
(30) van der Veken, B. J.; DeMunck, F. R. *J. Chem. Phys*. **1992**, *97*, 3060.
(31) Bulanin, M. O. *J. Mol. Struct*. **1973**, *19*, 59.
(32) Bulanin, M. O. *J. Mol. Struct*. **1995**, *347*, 73.
(33) Groner, P.; Johnson, R. D.; Durig, J. R. *J. Mol. Struct*. **1986**, *142*, 363.
(34) Botskor, I.; Hirota, E. *J. Mol. Spectrosc.* **1976**, *61*, 79.